University of Alberta

Remediation of Flare Pit Soil Using Supercritical Fluid Extraction (SFE)

by

Vaishalie Nagpal ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Master of Science

in

Environmental Science

Department of Civil and Environmental Engineering

Edmonton, Alberta

Spring 2004

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 0-612-96525-2
Our file Notre référence
ISBN: 0-612-96525-2

The author has granted a non-exclusive license allowing the Library and Archives Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou aturement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

ABSTRACT

Supercritical fluid extraction (SFE) proved to be a promising new technology for remediation of flare pit soils. Two flare pit soils (one sand and one loam) were collected from sites in Alberta and investigated. Extraction experiments were conducted at conditions of temperature and pressure ranging from 40°C to 80°C and 11.0 MPa to 24.1 MPa, respectively, in an attempt to identify optimum extraction conditions. SFE was found to be solvent density dependent. Of the various extraction conditions investigated, a pressure of 24.1 MPa and a temperature of 40°C (highest supercritical fluid density) yielded the highest extraction efficiency for both the soils. These conditions led to 89% extraction efficiency for total petroleum hydrocarbons (C_{10} to C_{50}) for the sand and 80% extraction efficiency for the loam. An increase in temperature at a fixed pressure led to a decrease in the extraction efficiency while an increase in pressure at a fixed temperature led to an increase in the extraction efficiency. The treated soils appeared to be drier, grainy and lighter coloured than the soil prior to extraction.

ACKNOWLEDGEMENTS

I would like to deeply thank and acknowledge my supervisor, Dr. Selma Guigard for her constant support and valuable advice not only throughout the course of this project work and making it a success but also otherwise. Your suggestions and advice are greatly appreciated. Thank you for giving me the opportunity to pursue this research, for all your encouragement that always boosted my confidence, and most importantly for your faith in me. I would also like to thank Dr. Feral Temelli and Dr. Warren Kindzierski for agreeing to be on the examining committee for my defence.

The interest and support provided by Imperial Oil Resources Ltd. by funding this project is greatly acknowledged. Special thanks are extended to Dr. Julie Roy and Tine Schaffer at Imperial Oil Resources for their help and valuable input during this project.

The assistance and guidance provided by the technicians in the Department of Civil and Environmental Engineering are also sincerely appreciated. Nick Chernuka, Garry Solonynko, Debra Long and Maria Demeter were always there to help me set up equipments in the lab and operate them. Thank you for all your time and effort. Also, I would like to acknowledge the immense technical and operational help provided by Darren Johnston (Varian Inc. Canada) on the functioning of GC/FID. Thank you very much for your patience, time and guidance.

I would also like to extend my special thanks to Olusegun Odusanya for making me understand and be comfortable with the operation of SFE apparatus. I also appreciate the valuable assistances provided by Jairo, Bernhard, and Luo in the lab. Thank you to all

the staff and students in the Department of Civil and Environmental Engineering for being friendly and supportive whenever I needed any help.

Last but not least, I would like to acknowledge my family (my mother, my father, my younger sister and brother) and thank them from the bottom of my heart for their love and support. Thanks for being understanding and patient with me at times when I was not the greatest person to be around. Thank you for always being with me!

I would like to extend my thanks to everyone else who has been helpful in any way towards the fulfillment of this project.

TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION 1
- 1.1 PROBLEM STATEMENT 1
- 1.2 OBJECTIVE 4

CHAPTER 2. LITERATURE REVIEW 6
- 2.1 FLARE PITS 6
- 2.2 ENVIRONMENTAL ISSUES RELATED TO FLARE PITS 7
- 2.3 REMEDIATION CRITERIA FOR FLARE PIT SOIL 13
  - 2.3.1. Alberta Tier I or Background 14
  - 2.3.2. CCME Criteria for Industrial Sites 14
  - 2.3.3. Alberta Tier II Criteria. 17
  - 2.3.4. Tier I a (UCASTG Criteria). 17
- 2.4 BACKGROUND 17
  - 2.4.1 Flare pit Waste – Characterization 19
  - 2.4.2 Flare pit waste/sludge – Treatment 21
    - 2.4.2.1 Solidification/stabilization 22
    - 2.4.2.2 Land treatment or land farming 23
    - 2.4.2.3 Biocell and Biopile Treatment 25
    - 2.4.2.4 Composting 26
    - 2.4.2.5 Bioremediation 28
    - 2.4.2.6 Thermal Treatment 32
- 2.5 SUPERCRITICAL FLUID EXTRACTION 35
  - 2.5.1 Current status of SFE and its role in soil remediation 39
    - 2.5.1.1 Effect of soil type 40
    - 2.5.1.2 Removal of Petroleum Hydrocarbons (PHCs) 43
    - 2.5.1.3 Removal of Polyaromatic hydrocarbons (PAHs) 46
- 2.6 SUMMARY 48

CHAPTER 3. MATERIALS AND METHODS 50
- 3.1 MATERIALS 50
  - 3.1.1 Flare pit soils 50
  - 3.1.2 Motor Oil and Weathered Diesel Oil 53
  - 3.1.3 Sand 54
  - 3.1.4 Chemicals 54
  - 3.1.5 Extraction vessel 55
  - 3.1.6 SC CO_2 Extraction Apparatus 58
- 3.2 METHODOLOGY 62
  - 3.2.1 SC CO_2 Extractions 63
  - 3.2.2 LabView 68
  - 3.2.3 Petroleum Hydrocarbon (PHC) Analysis 70
    - 3.2.3.1 Soxhlet extraction 72
    - 3.2.3.2 GC/FID method 74

CHAPTER 4. RESULTS AND DISCUSSION 86
- 4.1 SC CO_2 EXTRACTION OF PHC_S FROM FLARE PIT SOILS 86

4.1.1 Pressure Data 87
4.1.2 Flow Data 91
4.1.3 Temperature data 95
4.1.4 Visual Observations 98
4.1.4.1 Observations of the flare pit soils before and after SC CO_2 extraction 98
4.1.4.2 Observations of the extracted PHCs 98
4.2 PETROLEUM HYDROCARBON ANALYSES 100
4.2.1 Alkane Retention Time 101
4.2.2 GC/FID Calibration 103
4.2.3 GC Method Validation 109
4.2.4 Extraction efficiency 113
4.2.4.1 Extraction efficiency for specific PHC Fractions 120
4.2.4.2 Effect of Temperature 125
4.2.4.3 Effect of Pressure 127
4.2.4.4 Effect of Density 132
4.2.4.5 Effect of CO_2 flowrate 136
4.2.4.6 Effect of soil type 139
4.2.5 Chromatograms of PHCs 141
4.2.5.1 Untreated and treated Flare pit soils 141
4.2.5.2 PHCs trapped in glass vials during SC CO_2 extractions 143
4.26 Mass of PHCs collected 147
4.3 VARIABILITY IN RESULTS 149
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS 158
5.1 CONCLUSIONS 158
5.2 RECOMMENDATIONS 160
5.3 SUGGESTIONS FOR FUTURE WORK 161
CHAPTER 6 REFERENCES 162
APPENDIX A 171
APPENDIX B 180
APPENDIX C 211
APPENDIX D 214
APPENDIX E 217
APPENDIX F 219
APPENDIX G 235

LIST OF TABLES

Table 2.1: Canadian Soil Quality Guidelines and CWS for PHCs 16
Table 3.1: Characterization of Flare pit soils 53
Table 3.2: SC CO_2 extraction system components 61
Table 3.3: Supercritical CO_2 extraction experimental conditions 65
Table 4.1: Retention times of n-alkanes 103
Table 4.2: Linearity of single compounds (n-alkanes) obtained using 107
calibration Method 1and Method 2 107
Table 4.3: Linearity of F2, F3, and F4 fractions of motor oil calibration standards obtained using calibration Method 1 and Method 2 107
Table 4.4: RF values of n-alkanes obtained by running calibration standards 108
Table 4.5: GC analyses for calibration verification standards 110
Table 4.6: Sample analyses results obtained in the lab and in the commercial lab . 112
Table 4.7: Petroleum Hydrocarbon extraction results for FP 1 at 40°C 117
Table 4.8: Petroleum Hydrocarbon extraction results for FP 1 at 25°C, 60°C, and 80°C 118
Table 4.9: Petroleum Hydrocarbon extraction results for FP 2 at 40°C 119
Table 4.10: Petroleum hydrocarbon extraction results for FP 1 at 40°C 123
Table 4.11: Petroleum hydrocarbon extraction results for FP 1 at 60°C and 80°C 124
Table 4.12: Petroleum hydrocarbon extraction results for FP 2 at 40°C 124
Table 4.13: Results of PHC extraction from FP 1 using SC CO_2 double cycle extractions at 15.2 MPa and 40°C (SC CO_2 flow rate of 1 mL/min)...... 152
Table 4.14: Results of PHC extraction from FP 2 using SC CO_2 double cycle extraction at 14.8 MPa and 40°C (SC CO_2 flow rate of 10 mL/min) 153
Table 4.15: Raw flare pit soil analyses results obtained in-house and other laboratory 156

LIST OF FIGURES

Figure 2.1: Pressure-Temperature phase diagram of carbon dioxide 36
Figure 3.1: FP 1 (left) and FP 2 (right) used in the research 51
Figure 3.2: Pressure vessel cover (diagram supplied by Autoclave Engineers) 56
Figure 3.3: Schematic of pressure vessel cover 57
Figure 3.4: Lab-scale supercritical fluid extraction (SFE) apparatus 59
Figure 3.5: Lab-scale Supercritical fluid extraction (SFE) apparatus 60
Figure 3.6: Hydrocarbons collected every 5-minutes during dynamic extraction 67
Figure 3.7: Lab View Screen 69
Figure 3.8: Soxhlet extraction apparatus 73
Figure 4.1: Sample pressure data for a single-cycle SC CO_2 extraction 88
(at 15.2 MPa and 40°C , 2003-06-27) 88
Figure 4.2: Sample pressure data for a double-cycle SC CO_2 extraction 90
(at 20.7 MPa and 40°C, 2003-06-27) 90
Figure 4.3: Pump flow data for single-cycle (2003-06-27) extraction (full scale) 92
Figure 4.4: Pump flow data for single-cycle (2003-06-27) extraction 93
(reduced scale) 93
Figure 4.5: Pump flow data for double cycle (2003-08-02) extraction (full scale) 94
Figure 4.6: Pump flow data for double cycle (2003-08-02) extraction (reduced scale) 94
Figure 4.7: Temperature data for single cycle extraction (2003-06-27) 96
Figure 4.8: Temperature data for double cycle extraction (2003-08-02) 96
Figure 4.9: Flare pit soil 1 before and after extraction 99
Figure 4.10: Flare pit soil 2 before and after extraction 99
Figure 4.11: PHCs collected during SC CO_2 extraction 99
Figure 4.12: nC_{10}, nC_{16}, nC_{34}, and nC_{50} retention time chromatograms obtained using method 1 and method 2 102
Figure 4.13: GC/FID n-alkane (nC_{10}, nC_{16}, nC_{34}) standards calibration curves (Method 1) 104
Figure 4.14: GC/FID n-alkane (nC_{10}, nC_{16}, nC_{34}) standards calibration curves (Method 2) 105
Figure 4.15: Chromatogram of 5000 ppm motor oil calibration standard 109
Figure 4.16: Chromatograms of contaminated FP 1 (top) and FP 2 (bottom) showing PHC fractions F2, F3, and F4 114
Figure 4.17: Chromatograms of untreated real FP 1 and SFE treated flare pit soil at 24.1MPa and 40°C 116
Figure 4.18 : Effect of temperature at constant pressure (15.2 MPa) 127
Figure 4.19: Effect of pressure at different temperatures 128
Figure 4.20: Petroleum hydrocarbon fraction removal (%) for FP 1 at 40°C 131
Figure 4.21: Petroleum hydrocarbon fraction removal (%) for FP 2 at 40°C 131
Figure 4.22: Effect of SC CO_2 density on extraction efficiencies 133
Figure 4.23: Behavior of mass of PHCs collected during SC CO_2 extractions at 15.2 MPa and 40°C at different SC CO_2 flowrates (FP 1) 137

Figure 4.24: Behavior of cumulative mass of PHCs collected irrespective of amount of CO_2 flowing through the vessel at different flowrates (FP 1) 138
Figure 4.25: Chromatograms of untreated and treated FP 1 142
Figure 4.26: Chromatograms of untreated and treated FP 2 143
Figure 4.27: Chromatograms of Trap 1 (65 min), Trap 12 (180 min) and solvent Trap at 12.4MPa and 40°C for FP 1 144
Figure 4.28: Chromatograms of Trap 1 (65 min), Trap 6 (90 min) and Trap 12 145
(180 min) at 15.2 MPa and 80°C for FP 1 145
Figure 4.29: Chromatograms of Trap 1 (30 min), Trap 5 (210 min), Trap 9 (330 min) and bypass trap at 15.2 MPa for FP 1 147
Figure 4.30: Mass of HCs collected with time during SC CO_2 extraction at 24.1MPa for FP 1 148
Figure 4.31: Mass of HCs collected with time during SC CO_2 extraction at.............. 148
24.1 MPa for FP 2 148
Figure 4.32: Two SFE treated FP 1 soil samples obtained from Run 1 and Run 2 performed at 20.7 MPa and 40°C (layered on top of each other) 150

LIST OF ACRONYMS

AEP	Alberta Environmental Protection
AEUB	Alberta Energy and Utilities Board
ANOVA	Analysis of Variance
BOD	Biological Oxygen Demand
BTEX	Benzene, Toluene, Ethyl benzene, Xylene
CAPP	Canadian Association of Petroleum Producers
CCME	Canadian Council of Ministers of Environment
CO_2	Carbon Dioxide
CWS PHC	Canada Wide Standard for Petroleum Hydrocarbons
EC	Electrical Conductivity
EPA	Environmental Protection Agency
EUB	Energy and Utilities Board
FID	Flame Ionization Detector
FRTR	Federal Remediation Technologies Roundtable
GC	Gas Chromatograph
HCs	Hydrocarbons
MDL	Method Detection Limit
MOU	Memorandum of Understanding
PAHs	Polyaromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PHC	Petroleum Hydrocarbon
PHCs	Petroleum Hydrocarbons

PTAC	Petroleum Technology Alliance of Canada
RF	Response Factor
RSD	Relative Standard Deviation
SAR	Sodium Adsorption Ratio
SC CO_2	Supercritical Carbon dioxide
SCF	Supercritical Fluid
SD	Standard Deviation
SFE	Supercritical Fluid Extraction
SQG	Soil Quality Guidelines
TOC	Total Oxygen Demand
TPH	Total Petroleum Hydrocarbons

CHAPTER 1. INTRODUCTION

1.1 PROBLEM STATEMENT

The advancement in industrial sector and technology has led to an increased interest in the remediation of land contaminated as a result of the industrial activities, spills, and improper storage and disposal of wastes. There are possibly tens of thousands of contaminated sites in Canada (NRTEE 1997). Many of these sites are contaminated with petroleum hydrocarbons (PHCs). In some cases, these PHCs may be biorecalcitrant-non-agreeable to biological treatment methods, and therefore the soils contaminated with these PHCs are not amenable to remediation by biological treatment methods.

Examples of sites containing biorecalcitrant PHCs are old flare pit sites. Flare pits are earthen pits that were once used for the storage and disposal of natural gas and crude oil wastes. Alberta's oil patch contains thousands of flare pits that may need remediation and reclamation. At some sites, the soils in and around the flare pits are highly contaminated with biorecalcitrant PHCs that current remediation technologies such as bioremediation and, more rarely, composting, may be limited. High concentrations of PHCs along with other contaminants such as brine and metals could influence the microbiological processes in the soil, thereby affecting the soil quality. These contaminants may leach into the ground water, inhibit microbial activity, and may reduce the soil micro flora and fauna, thereby posing a threat to the surrounding environment and consequently to human health. Remediation of sites containing high concentrations of biorecalcitrant petroleum hydrocarbons (PHCs) is usually performed by means of excavation and landfilling.

Very few studies dealing with the remediation of flare pit soils have been published. Current technologies include backfilling the pit with clean material or excavation followed by land treatment such as landfilling, thermal treatment, bioremediation or composting (Amatya et al. 2002; Chaw and Stoklas 2001; Catalan et al. 1998; EUB 1996-b). A simple dilution of the contaminants and their possible transfer to a new site, thereby increasing the contaminant levels in non-affected areas of land is becoming a larger land management issue (Speer 1999). Both excavation followed by landfilling and thermal treatment can be implemented relatively quickly, but they can be costly. In the case of thermal treatment, the process may adversely affect the quality of the soil. For example, Catalan et al. (1998) found that, after thermal treatment, the treated soil contained high levels of salts and had a very low pH, indicating production of acidic compounds during the treatment process. In addition, thermal treatment may lead to the formation of toxic air contaminants that require treatment before release to the atmosphere (Catalan et al. 1998). With respect to bioremediation and composting, although these processes have the advantages of being non-invasive and relatively cost efficient, both technologies can be slow and time-consuming (Riser-Roberts 1998). Thus, there is a need to develop fast, cost effective, alternative technique for remediation of contaminated soil. New, more effective treatment technologies are therefore being investigated to treat these types of soils.

Supercritical fluid extraction (SFE) is currently being investigated as a solvent extraction process for the remediation of contaminated soils and may potentially be applicable to the remediation of flare pit soils. SFE has shown to be an attractive alternative to solvent extraction due to the better mass transfer and solubility characteristics of supercritical fluids (SCFs), shorter extraction times and ease of extract separation. In SFE, the recovery of the contaminant from the soil requires maximizing the solubility of the contaminant in the SCF compared to that in the soil matrix, and consequently maximizing its mass transfer from the soil matrix to the SCF. In the supercritical state, supercritical solvents are extremely sensitive to small changes in temperature and pressure such that a solute may be extracted from a matrix at one set of conditions and completely separated from the solvent in a downstream operation at slightly different conditions (Tomasko et al. 1995).

Various studies have investigated the use of SFE for removing toxic organic compounds from contaminated soils. SFE has been used to recover petroleum hydrocarbons (PHCs), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs and dioxins), phenols, chlorinated phenols, metals, and many pesticides and herbicides from contaminated soil, sediment and other environmental matrices (Bjorklund et al. 1999; Chen et al. 1997; Lee and Gongaware 1997; Low and Duffy 1995; Laitinen et al. 1994; Eckert-Tilotta et al. 1993; Lopez Avila et al. 1993; David et al. 1992; Laintz et al. 1992; Hess et al. 1991; McNair and Frazier 1991; Dooley et al. 1990; Brady et al. 1987).

No work related to the extraction of PHCs from flare pit soils using SC CO_2 has been published to date. To our knowledge this will be the first published work on the remediation of flare pit soil using SFE. The research described herein focuses primarily on the use of a laboratory scale SFE system to investigate the extraction of PHC fractions

F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}), and F4 (nC_{34}-nC_{50}) from contaminated flare pit soils at various temperature and pressure conditions in an attempt to determine the best extraction conditions, and in an attempt to determine the effects of pressure, temperature, CO_2 flowrate and soil type on the extraction efficiency. However, the primary focus of this research is F4 fraction of PHCs, which are heavier PHCs that are difficult to treat and degrade. The obtained results will provide the necessary information for potentially developing SFE as a fast and effective technology for remediation and decommissioning of flare pits in Alberta and elsewhere in Canada.

1.2 OBJECTIVES

The objective of this research project was to use the laboratory scale SFE system to investigate the extraction of petroleum hydrocarbon fractions in particular CCME fractions F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}), and F4 (nC_{34}-nC_{50}) from contaminated flare pit soils at various conditions of temperatures and pressures, ranging from 40°C to 80°C and 11.0 MPa to 24.1 MPa, respectively. Two soils (one sand and one loam) were collected from two sites in Alberta, and were investigated in this work. The primary goal of this project was to bring down the petroleum hydrocarbon concentration in the SFE treated flare pit soil, such that it meets the *Federal Soil Quality Guidelines* for PHC contaminated coarse-grained and fine- grained soils as set by the Canadian Council of Ministers of Environment (CCME 2001a; CCME 2001b). In addition, the focus of this research was the extraction of F4 fraction of PHCs, which are heavier PHCs that are difficult to treat and degrade. The effects of different pressures and temperatures, CO_2 flow rates, and soil type on the extraction efficiency of the process were also investigated.

Chapter 2 of this work presents the background information and issues related with flare pits, the remediation criteria as set by CCME for PHC contaminated soils and a review of the current technologies being used for the treatment of flare pits. Chapter 2 will also provide a detailed review of SFE as a soil remediation technology. The literature review will then be followed by Chapter 3, which presents the methodology used for extractions performed in this work and their analysis. The results and discussion will then be presented in Chapter 4, followed by conclusions and recommendations presented in Chapter 5.

CHAPTER 2. LITERATURE REVIEW

2.1 FLARE PITS

There are several thousands of flare pits in Canada. According to recent estimates, Alberta alone is home to about 30,000 flare pits (Speer 1999). Flare pits are earthen pits that were commonly used by the upstream oil and gas industry for the storage and disposal of oil field wastes and for the handling of wastes resulting from process upsets. The primary purpose of flare pits was to store and effectively burn hydrocarbons and produced fluids directed to them from oil and gas operations. Produced fluids include crude bitumen, liquid hydrocarbons, process chemicals, or water produced from gas wells, oil wells, associated batteries, and processing facilities (CAPP 1996). Most flare pits are usually unlined excavations, which contain sludge produced due to the above-mentioned handling and disposal practices. Flare pit sludge shows great variability in characterization from pit to pit, and the leaching of contaminants from some of these pits poses a threat to workers, ground water, and surrounding flora and fauna.

Flare pits are often found at older sites, compressor stations, and pumping batteries throughout Alberta (Green 1997). The blowdown operations and process upsets at the site were connected to flare pits using a low-pressure line, called a flare line. This flare line caused excess gas and fluid to enter the flare pit when process upsets or blowdown operations occur at the site. Some flare lines were equipped with a burner tip at the end of the line, which provided thermal destruction of the material exiting the flare line. Flare pits were also used for direct addition of material when they were used for storage of bulk production fluids including crude oil, process chemicals and process water. Spill material and other site wastes had also been directed into flare pits as means of disposal. These pits were often built to manage process upsets in heavily forested areas as an alternative to a flare stack that might pose threat to the surrounding environment. Thus, flare pits provided a means for storage of wanted and unwanted materials generated during oilfield/ crude oil processing.

2.2 ENVIRONMENTAL ISSUES RELATED TO FLARE PITS

As of December 1996, the provincial government of Alberta has banned the use of these flare pits, and has requested that the oil and gas industry remediate the former flare pit sites that pose a threat to the surrounding environment and/or to human health (AEUB 1996a). Remediation and reclamation of flare pit sludges and surrounding soil are regulated by Alberta Environment Protection, while the Alberta Energy Utility Board (AEUB) is taking steps to reduce the use of flare pits/ponds at upstream oil and gas facilities (AEUB 1996a) . The nature of their use and the recognition that they should no longer be used suggest that flare pits are of primary concern related to environmental contamination at older oil and gas well sites. Depending on the type and extent of contamination, the presence of flare pits reflects the waste management practices that were followed and are unacceptable according to the current standards set by regulatory bodies, the general public and industry (Marr-Liang 1999). According to Speer (1999), these past management practices symbolizes a cost for clean-up ranging from minimal to major again depending on the type and extent of contamination.

It is believed that most of the flare pits are decades old with certain ones being 20 to 30 years old, since drained and buried (Cook et al. 2002). Flare pit soils have irregular consistencies in terms of texture and porosity, and some are impacted with inorganic co-contaminants such as heavy metals and brines in addition to PHCs. Flare pit waste may contain high molecular weight hydrocarbons and recalcitrant compounds that are not easily biodegradable. The above-mentioned characteristics of flare pit soils make them particularly difficult to remediate (April et al. 2000). Factors such as lack of bioavailability due to soil adsorption, lack of necessary oxidizing enzymes, possible steric hindrance for enzyme attack and toxicity to the soil microorganisms, low solubility, soil characteristics, and type of PHCs may contribute to the apparent recalcitrance of PHC fractions (Amatya et al. 2002). The soil present in the weathered flare pits have a high degree of partitioning of PHCs to the soil organic carbon, which reduces the solubility and hence the degradability of these hydrocarbons (Cook et al. 2002). The binding of PHCs to the soil is largely influenced by the nature of the soil (textural class and organic matter content, for example. It is suggested that lightweight hydrocarbons (HCs) if present have greater mobility than heavy HCs, thereby spreading much further and easily in the soil as compared to heavier HCs. It is the mobility and the bioavailability of the hydrocarbon contaminants rather than the total hydrocarbon contamination, which determines the environmental impact of soil contamination (Cook et al. 2002). Metal contamination can also be found in different forms where metals are found in adsorbed, exchangeable, reducible or bound to carbonate phase in the soil; the bioavailability and toxicity of which depends on the degree of sorption to the soil (Cook et al. 2002). Also, the permeability of the soil might affect the migration of contaminants into groundwater (Speer 1999). Although most HCs at low concentrations do not have high toxicity, they may pose an aesthetic nuisance (Green 1997). However, it might be important to have knowledge of the hydrocarbon chain lengths, which can provide an insight into the toxicity of the site as soil quality and remediation potential are related to different fractions of HCs with short, medium and long chain lengths (Speer 1999). A recently released newsletter by Petroleum Technology Alliance of Canada, PTAC (PTAC 2003) acknowledges the potential of interactions between different fractions of PHCs. These interactions are assumed to be additive or might be less-than additive (antagonistic). Further investigation in this study is under progress. Moreover, aging of HCs does not seem to reduce the bioavailability and hence the toxicity of the HCs present in the contaminated soil (Cook et al. 2002). Since, the contents present in the pit are contained in a material that is either liquid or semi-liquid form, contaminants may impact the flare pit and negatively impact the site vegetation by migrating outward in the site (Speer 1999). In spite of having fences around some of the flare pits for security, the pits can still be accessed by wildlife and can pose hazard to workers at site.

A number of negative environmental effects of hydrocarbons have been identified on soil and sub-surface environment, a detailed qualitative review of which is presented by Rowell (1992). These include:

Reactions at the soil surface - The surface areas affected by hydrocarbons are largely governed by the specific gravity, viscosity, and temperature of the hydrocarbons. Evaporation and chemical weathering could also be significant processes responsible for the loss and change in HCs. Other health risks of concern from exposure to soil surface contaminated with HCs involve an explosion, fire, skin contact and inhalation particularly during burning operations, or when HCs are being actively discharged. 'Flashing' may also occur due to the reaction of mixing of volatile constituents of hydrocarbon liquid with air forming potentially explosive mixtures (Rowell et al. 1992).

Hydrocarbon movement into the soil - The geometry of the soil, presence of adsorbing surfaces and soil moisture governs the transport and movement of HCs within the soil. Initially, the movement of hydrocarbons within a soil is a multiphase flow with oil and water phase immiscible. Biological decomposition and abiotic weathering emulsifies and solubilizes the HCs to become associated with water phase. Attachment to more mobile constituents of soil may increase the mobility of the HCs. However, in dry soils, internal volatilization and vapor movement may also be significant. The rate of hydrocarbon movement depends upon the density and viscosity of oil, soil moisture, surface adsorption, wetting characteristics, and presence of large continuous pores (Rowell et al. 1992).

Reactions with soil organic matter – Strong adsorption of hydrocarbons onto the organic matter not only may result in reduced rates of volatilization and biodegradation but also may affect the rates of hydrolysis, photolysis and bioaccumulation of hydrocarbons. Chemical reactions with soil organic matter may result in reduced solubility and increased stability of hydrocarbons in soil, and these reactions depend on the molecular size and polarity of the compound involved (Rowell et al. 1992).

Hydrophobicity - A variety of effects related to wet subsoils, and dry soil surfaces might occur due to oil-induced hydrophobicity. Increased water run off and lateral movement of hydrocarbon compounds may be found on sloping land due to surface hydrophobicity as a result of which, a decrease in soil wettability may occur leading to complete desiccation and loss of soil structure, thereby making soil more susceptible to wind and water erosion. On the other hand, presence of HCs may also reduce the potential for wind and water erosion by increasing the size and water stability of soil aggregates. Adverse hydrophobic conditions may last for many years depending on the nature of soil, type of hydrocarbons and remediation practices (Rowell et al. 1992).

Aeration, soil moisture and soil temperature - Proper plant growth and aerobic biological processes require air movement through the soil matrix. The presence of hydrocarbons in void spaces makes it difficult to maintain aerobic conditions needed for microbial growth. Hydrocarbons present in soil voids reduce the soil air volume by displacing the air present in the soil's void spaces and resulting in anaerobic conditions in the soil. Many oil field spill sites are found to have anaerobic soil conditions (Green 1997). The hydrophobic effect of HCs and the soil surfaces may also change the moisture availability in the soil. Soil temperature within the soil is less variable than air temperature. Oily materials modify temperatures at the surface and within the soil by increasing the absorption of solar radiation and by eliminating surface vegetation, darkening the surface and drying the soil. Dark colored HCs such as crude oil, bitumen, and asphalt cause large increases in surface temperatures in the soil (Rowell et al. 1992).

Biological effects - Some of the important microbes existing in the soils include bacteria, yeasts, filamentous fungi, algae and protozoa (Rowell et al. 1992). It has been found that different HCs exhibit varying levels of toxicity, and the target organisms show varying degree of tolerance to the HCs. Both direct and indirect effects (related to nutrition, aeration, pH, moisture uptake, and hydrocarbon movement through the soil) on microbial growth are involved. Although the addition of HCs may increase the total microbial activity, the overall number of microbial species present may be reduced. The decomposition of carbon-rich oily material/HCs may result in a deficiency of nutrients required for microbial growth. The deficiency includes a deficiency of nitrogen along with shortages of phosphorous, sulfur, potassium, calcium, magnesium and trace elements. Soil invertebrates such as nematodes, earthworms, mites, snails, millipedes and spiders are also affected by HCs, where earthworms and nematodes are used as indicators of soil toxicity. It was found that nematode population decreased by 60-90% as compared to control soils after 12 months of treatment with a variety of HCs (Rowell et al. 1992).

Direct or indirect plant damage can also occur due to excessive contact with HCs. The more susceptible plants include seedlings, annual species, and plants with large leaf intercepting surface areas, shallow roots or no roots, or those with thin leaf cuticles. Direct contact of HCs may damage the cell membranes, thereby preventing seed germination. Indirect effects on plant growth relate to reactions between soil and HCs, consequences of enhanced microbial growth on HCs, or due to decreased aeration, poor water absorption, and soil waterlogging at depth. A competition for the uptake of available nutrients such as nitrogen between plants and oil-degrading microbes results in poor growth or death of plants unless soil is supplied with the required nutrients (Rowell et al. 1992).

Usually high levels of salinity and sodicity are accompanied with flare pit sites contaminated with HCs. Excessive salinity and sodicity can degrade soil's physical properties and affect its ability to support plant growth. Ion toxicity effects (e.g. excessive Na^+, Cl^-), and nutritional imbalances (e.g. excessive uptake of Na^+ or K^+ relative to Ca^{2+} or Mg^{2+}) may adversely affect plant growth. Salinity can be hazardous to plants if the soil's electrical conductivity (EC) exceeds 12 dS/m even at depth (Green 1997). However, sodicity can also degrade soil structure due to its dispersing effect on clay and organic colloids. Dispersed soils have poor structure, resulting in surface crusting, cementation and soil erosion. Sodicity can be managed using gypsum if the soil adsorption ratio (SAR) is between 6 and 10 (Green 1997).

2.3 REMEDIATION CRITERIA FOR FLARE PIT SOIL

Canadian Association of Petroleum Producers, CAPP (1996) describes the remediation criteria to be used for the reclamation of flare pits and ponds in Alberta. These include: Alberta Tier I Criteria for Contaminated Soil Assessment and Remediation, Canadian Council of Ministers of Environment (CCME) Criteria for Industrial sites, Alberta Tier II Criteria, and Tier Ia (UCASTG Criteria).

2.3.1. Alberta Tier I or Background

Alberta Environment Protection (AEP) developed provincial soil quality guidelines, Albert Tier I Criteria for remediation of contaminated soil is based on the conservative risk assumptions (Speer 1999). Alberta Tier I values are generic and represent the acceptable concentrations of contaminants in soil based on estimated soil background levels. These values apply to the entire province without restricting land use. The soil criteria include pH, EC, SAR, metals, monocyclic aromatic compounds, chlorinated HCs, and total extractable HCs (AEP 1994). In accordance with the National Guidelines for Decommissioning Industrial Sites, AEP subscribes to a two-tier approach to set acceptable concentrations of contaminants in soil (AEP 1994). Of this two-tier approach, Tier I criteria have been developed from the scientific literature, and from existing guidelines and current practices in Alberta and other political jurisdictions in Canada and abroad. Tier I requires appropriate site background sampling prior to conducting a clean up approach as in some cases natural background concentration of some contaminants may exceed Tier I levels (CAPP 1996).

2.3.2. CCME Criteria for Industrial Sites

The Canadian Council of Ministers of Environment (CCME) has established site remediation criteria (soil quality guidelines or SQGs) for sites zoned based on four generic land uses. In other words, CCME SQGs have put forward generic values for maximum allowable concentration of the contaminants according to the land use. These guidelines are documented as the Canada-Wide Standard for Petroleum Hydrocarbons (CWS for PHC). The CWS for is designed for the assessment and remediation of contaminated sites, and is expected to replace the many different analysis methods previously used by various laboratories and jurisdictions in Canada (CCME 2001c). The CWS for PHC (CCME 2001a) is developed as a remediation standard that sets out the PHCs levels to which a contaminated site should be cleaned up to- if and when they are subject to remediation. The CWS PHC is a remedial standard for contaminated soil and sub-soil occurring in four land use categories: agricultural, residential/parkland, commercial, and industrial developed for protection of human, and ecological health. Alberta Environment Protection (AEP) supports the CCME criteria assuming that the future land use will remain zoned industrial/commercial (CAPP 1996).

The framework of CWS for PHC includes three 'tiers' that are based on science of risk assessment, and require high levels of environmental and human health protection. These three 'tiers; are: Tier 1-generic numeric values; Tier 2 – adjustment to Tier 1 levels based on site-specific information; Tier 3 – site specific risk assessment (CCME 2001a). CCME Tier 1 levels for each land use are derived through a systematic evaluation of all exposure pathways applied to receptors of concern identified under that land use (CCME 2001a). CCME Tier 1 values are values generated for both human health and ecological protection such that both are protected when Tier 1 levels are applied. If no exceedances are found in Tier 1 assessment for particular land use site, investigation ceases and the site can be declared compliant with respect to CWS PHC (CCME 2001a), otherwise the site must be remediated to eliminate exceedances. Table 2.1 shows the acceptable values for industrial soil such as for EC, SAR and PHCs concentration in the coarse-grained surface soil (collected at <1.5m depth) and fine-grained sub soil (collected at >1.5m depth) in order to meet CCME criteria of soil quality (CCME 2001a; CCME 2001b).

Table 2.1: Canadian Soil Quality Guidelines for the protection of environmental and human health, and CWS for PHCs (CCME 2001a; CCME 2001b)

PARAMETER	COARSE-GRAINED SURFACE SOIL	FINE-GRAINED SUB SOIL
Electrical Conductivity (EC) (dS/m)	4	4
Sodium Adsorption Ratio (SAR)	12	12
Petroleum Hydrocarbon Content (PHC)*		
Tier 1 levels for surface soils		
F2 (C_{10}-C_{16}) mg/kg	760	3000
F3 (C_{16}-C_{34}) mg/kg	1700	5000
F4 (C_{34}-C_{50}) mg/kg	3300	10000

The land use category in this research work is industrial, and the '*Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method*' (CCME 2001c) is followed to analyze the PHC concentration present in the contaminated soil. According to the Canada-Wide Standard for Petroleum Hydrocarbons, the separate four fractions of PHCs should be determined analytically in order to decide if the site meets the acceptable criteria for various land uses. These four fractions are:

- F1 (nC_6 to nC_{10})
- F2 (nC_{10} to nC_{16})
- F3 (nC_{16} to nC_{34})
- F4 (nC_{34} to nC_{50})

2.3.3. Alberta Tier II Criteria.

Many companies use site-specific risk assessment approaches. Alberta Tier II criteria are site-specific, concerning protection of human health and the environment. Such criteria are based on acceptable human health and ecological risk specific to the site, in consideration of variables such as type of soil, geology, surface water and groundwater, climate and land use (AEP 2001; CAPP 1996).

2.3.4. Tier I a (UCASTG Criteria).

Currently the Upstream Chemically Affected Sites Task Group (UCASTG) is developing more generic remediation criteria for industry members, which depend on the location of the facility, nature of the contaminants and the potential receptors. This approach relates specifically to the conditions expected at oil and gas well facilities than a Tier I approach that is performed without a site-specific detailed risk assessment (CAPP 1996).

2.4 BACKGROUND

According to Alberta Energy and Utilities Board, (AEUB 1998), "Contaminated soils, sludges, and waters that are physically removed or excavated (from where the waste originated as a result of decontamination activities (e.g. earthen pit/pond reclamation, spill reclamation, underground, and above ground tank reclamation, etc.) are considered *oilfield wastes*". All oilfield wastes that are generated as a result of suspension, abandonment, decontamination, and surface land reclamation of active or inactive upstream oil and gas facilities fall under the jurisdiction of the AEUB. AEUB requires that all oilfield wastes (including flare pit waste) must be managed as an *ex-situ* treatment/disposal option in accordance with Energy and Utilities Board (EUB) Guide 58, '*Oilfield Waste Management Requirements for the Upstream Petroleum Industry*' (AEUB 1996b) and the Memorandum of Understanding (MOU) released as an Informational letter –IL 98-02 on March 26, 1998 (AEUB 1998). These options include one-time on-site land treatment of flare pit waste. Clean up of flare pit waste is a joint effort of AEP and AEUB. The MOU released in 1998 (AEUB 1998) described the roles of both organizations in the flare pit reclamation process. AEUB ensures that the storage of the flare pit waste occurs in accordance with EUB Guide 55 for management of storage waste (AEUB 2001), and that the *ex-situ* remediation or off-site disposal meets the requirement as per EUB Guide 58 (AEUB 1996b), while the remediation activity and standards for the soil and groundwater remediation of flare pits are regulated by AEP (AEUB 1998).

Since the problems associated with oilfield waste management were identified, many research projects in the area of remediation of flare pits and other contaminated solids from oil field operations in Western Canada have been carried out (Peake 1985). These studies often involved material classification followed by an evaluation of treatment technologies. Wotherspoon and Bromely (1989) conducted a study in 1989 for the Canadian Association of Petroleum Producers (CAPP), which described that flare pit sludge contains hydrocarbon waste materials. The goal of their study was to characterize all major types of wastes associated with upstream oil and gas sector, and to determine current and future disposal options. The study revealed that flare pit sludge was handled by a combination of on-site recycling, open pit burning, licensed oilfield waste reclaimers, and road application (Wotherspoon 1989). However, industrial landfill, solidification and incineration were preferred management practices at the time of the study (Wotherspoon 1989). Proper landfill design and management can limit mobility of the metals, organics and salts contained in the sludge. Mobility of contaminants may also be limited by solidification of the sludge using lime or cement, but the resulting solidified material may still require disposal in an area as fill or construction material. Incineration or thermal decomposition of flare pit sludge focuses on the organic content present in the sludge leaving behind metal and salt contamination as originally present in the pit sludge. Current treatment practices for the remediation of flare pit sludge includes excavation followed by a one time land treatment such as bioremediation, composting, and thermal treatment. The following sections describe flare pit sludge characterization and the current remediation technologies being used with their advantages and disadvantages.

2.4.1 Flare Pit Waste – Characterization

Green (1997) developed a database of 338 sites from oil and gas well facilities, 75% of these were flare pits. The database included site characteristics and soil quality data, the parameters of which were compared to the *Alberta Tier 1 Criteria for Contaminated Soil Assessment and Remediation* (AEP 1994). It was determined that 70% of the total flare pit samples exceeded hydrocarbon guidelines (>1000 ppm measured as oil and grease), 44% exceeded SAR guidelines, and 48% exceeded EC guidelines as per the Alberta Tier 1 Criteria (AEP 1994). The number of samples exceeding metal guidelines was small, mercury being the metal that caused non-compliance in 23% of the sites.

Speer (1999) constructed a larger database that included 436 flare pit sites in Western Canada, predominantly in Alberta. The sludge samples collected from these sites were characterized for significant parameters such as EC, SAR, pH, metals and hydrocarbons measured as oil and grease. These characteristics were then compared to the provincial and federal soil criteria. It is estimated that Alberta hosts about 30,800 flare pits and drilling sumps, and the database constructed by Speer (1999) represents only 1.4% of the total number of estimated flare pit sites in Alberta (Speer 1999). Although this percentage appears low, the database covers a significant portion of the sites in the province of Alberta.

In the study conducted by Speer (1999), it was determined that 27% of the total flare pit sites in Alberta met the provincial (Alberta Tier 1) and federal (CCME Soil Quality Guidelines) soil quality guidelines and therefore would not require remediation of the sites. However, 62% of the total samples analyzed for HCs exceeded the provincial soil remediation guidelines while 59% of samples exceeded the BTEX (Benzene, Toluene, Ethyl benzene, Xylenes) levels as required by the federal soil remediation guidelines. These results were similar to those obtained by Green (1997), where it was determined that more than half of the sites suffered from exceedances with respect to hydrocarbon concentrations based on Alberta Tier 1 criteria. Similarly, 46%, 52% and 20% of the total samples analyzed for EC, SAR and pH values, respectively, were determined to be exceeding the provincial soil remediation guidelines. For sites in exceedances with the metals such as arsenic, barium and mercury were found to be in high concentrations, mercury showing the most exceedances. However, many samples in the database lacked analytical data on metals (Speer 1999). Speer (1999) suggested that all the historical operational practices such as brine and hydrocarbon spills, open pit burning, temporary storage of HCs in open, non-lined pits, tank cleaning followed by on-site burial of tank bottoms and waste disposal using on-site pits contributed to the various types of contamination, consequently leading to different characteristics of the flare pit sites.

An oilfield waste characterization study was conducted by Wotherspoon (1989) on six waste sludges. One of the six sludges was flare pit sludge, which was defined as solids collected from the bottom of the pits found at batteries, fieldgates and wellsites not tied into flowlines. Three samples of the flare pit sludge were assessed for a total of 37 parameters, which included biological oxygen demand (BOD), total organic carbon (TOC), phosphorus, nitrogen, %solids, %water, oil and grease content, sulfur, specific gravity, pH, EC, particle size, free liquids, flash point, flammability, soluble cations and anions, and leachable metals. It was found that the three samples of flare pit sludge analyzed showed variability in almost all parameters. Also, the BOD results as obtained showed that the sludge was not very biodegradable.

2.4.2 Flare pit waste/sludge – Treatment

As mentioned earlier, very few studies dealing with the remediation of flare pit soils have been published. Based on EUB Guide 58, '*Oilfield Waste Management*

Requirements for the Upstream Petroleum Industry' (EUB 1996), non-refined hydrocarbon contaminated soil or pit/pond sludge on an active oil and gas site can be managed using treatment and disposal methods such as solidification/stabilization, or biodegradation techniques such as land treatment, bioremediation using biocell/biopile treatment, or composting. Other treatment methods include incineration, thermal oxidation, thermal desorption, thermal phase separation and thermal distillation recovery methods for the treatment of oilfield waste (pit/pond sludge). The highly complex and variable nature of flare pit waste presents a serious challenge to the remediation of flare pit sludge. In addition, the variability in the characteristics of the flare pit waste from one pit to another increases the uncertainty associated with the treatability. However, the permitted treatment and disposal methods for any type of oilfield waste, at any place, depend on the disposal regulations established by AEUB (1996b).

2.4.2.1 Solidification/stabilization

Solidification and stabilization refers to the waste fixation processes so as to immobilize, encapsulate or physically bound the waste contaminants in a solidified form in order to prevent soil and groundwater contamination. While solidification involves production of solids (using cementing material such as cement or lime kiln dust, fly ash or lime to provide high structural integrity to allow transport and disposal), stabilization involves reducing or ceasing the mobility of contaminants by the formation of insoluble compounds through reactions between stabilizing agents and contaminants (Riser-Roberts 1998; Lloyd and George 1994).

The primary limitations of this technology have been the negative effects of salts and hydrocarbons on the integrity of the stabilized waste matrix, as they are physically rather than chemically bound. Solidification is a viable, relatively simple disposal option; however, it is more expensive than land treatment or simple dilution burial (Lloyd and George 1994).

2.4.2.2 Land treatment or land farming

Land treatment or landfarming is a viable bioremediation technique used in the oil and gas industry for the treatment and disposal of non-refined hydrocarbon contaminated soils resulting from spills/leaks and non-refined hydrocarbon contaminated pit/pond sludges (EUB 1996). Land treatment involved the use of soil incorporation, dilution, chemical alteration, and biodegradation in a controlled manner to reduce contaminants to acceptable levels consistent with the intended land use (Lloyd and George 1994). In other words, it is a planned and control mixing of waste and surface soil to enhance the biodegradation, transformation or assimilation of the contaminants by inherent soil processes and convert them into carbon dioxide and water (Riser-Roberts 1998; EUB 1996). The fact that the soil tends to hold the HCs (in the form of oil) in place and provide large surface areas for its metabolism is an important advantage offered by land treatment for HC biodegradation. Land treatment is a one-time application process, i.e. it is limited to the situation where non-refined HC contaminated soils are land treated in a single application of the waste (AEUB 1996b). It is an active practice where biodegradation of HCs may be enhanced by application of nutrients and frequent tillage (to increase aeration) of the mixture. Thus, only wastes susceptible to biodegradation should be land treated. Soil conditions are often controlled to optimize the rate of contaminant degradation. These conditions include moisture content (usually by irrigation or spraying), aeration (by tilling the soil with a predetermined frequency, the soil is mixed and aerated), pH (buffered near neutral pH by adding crushed limestone or agricultural lime), and other amendments such as soil bulking agents, nutrients, etc. (FRTR 2002).

An eight year study carried out from 1982 to 1989 on the efficiency of land treatment of oilfield wastes, determined that land treatment can be used as a remediation technique for oilfield wastes from a variety of locations in Alberta, and that proper management of the land used for treatment can lead to its use for future agricultural purposes (Danielson 1990). The study concluded that HC degradation (HCs occurring in the form of oil) occurred primarily through microbial degradation. The highest oil degradation rates were observed during the first year of sludge application, and decreased thereafter. Asphaltene concentration was expected to remain constant during the treatment and slow down the oil degradation rate. It was determined that HC levels (in the form of oil) in the soil below 3.5% did not affect the plant growth, whereas plant growth was inhibited at soil oil levels at or greater than 5%. Also, no uptake of trace organics was found by the plants grown on the land treatment facilities, thereby concluding no health risk from consumption of these plants (Danielson 1990).

Land farming has been proved to be a successful treatment technology for the removal of PHCs from weathered crude oil contaminated soils, resulting in 96% biodegradation of compounds with carbon numbers from 10 to 20, and 85% biodegradation of compounds with carbon numbers above 44 (Riser-Roberts 1998). Land farming is simple, inexpensive and requires no process control or skilled personnel. However, it requires large amounts of time and land, continuous monitoring, and good operation and maintenance of the site to achieve proper results. The process is also sensitive to weather conditions such as rainfall, wind, temperature etc. that are uncontrollable, and often increases the length of time to achieve remediation. Land treatment poses a risk to surface and groundwater quality through surface water runoff or leaching (FRTR 2002; Riser-Roberts 1998).

2.4.2.3 Biocell and Biopile Treatment

Biocell or biopile treatments are alternatives to land treatment, where oilfield wastes are biologically degraded in a contained and controlled environment. The main difference between a biopile and a biocell is that a biopile is constructed on the ground surface and the waste material is laid down as piles on an impervious liner, while a biocell consists of a walled containment system built on or below ground surface. Excavated soil is placed in the treatment area in an impermeable cell structure or piled on an impermeable liner. The piles are often covered to prevent loss of any off-gases such as volatile organics or carbon dioxide (one of the products of microbiological catabolic processes) to the atmosphere during the process. The soil during treatment is periodically turned over to provide aeration, and water, nutrients and oxygen can be added in a controlled manner using a sprinkling system or perforated pipes. Application of soil conditioners such as sawdust, straw, or manure can improve the soil texture and increase soil permeability. The ability to control moisture prevents soluble contaminants from leaching (FRTR 2002; EUB 1996). According to EUB (1996b), biocell and biopile treatment should be used when site conditions are not suitable for land treatment, or when the waste volume prevents one-time on-site application. These treatment technologies should be of particular interest if the waste is intended to be used as fill material after successful biodegradation, and if biodegradation is an intermediate step to make waste suitable for another treatment disposal option (EUB 1996). Biocell and biopile treatment units require smaller areas than land farming, and optimal treatment conditions can be maintained and controlled to reduce the treatment time needed.

2.4.2.4 Composting

Composting is a solid phase biological treatment method used as an alternative to landfarming for bioremediation of weathered HCs (Chaw and Stoklas 2001; Riser-Roberts 1998). The excavated soil is piled and mixed with bulking agents such as wood chips, straw, manure, leaves, rice hulls or other materials to increase porosity. The soil is tilled periodically to provide aeration. The biological decomposition of organic material occurs under controlled conditions of moisture, nutrient and pH levels. The process involves the activity of a succession of mesophilic and thermophilic microbes. Nitrogen and phosphorus based fertilizers, as well as trace minerals may be added to enhance microbial activity (Riser-Roberts 1998). Composting is considered safer than landfarming as the material is contained in a containment structure rather than being spread or worked into the land. Another advantage of composting over land treatment is the greater control over the environmental conditions of importance to microorganisms such as nutrition, temperature, moisture content and other factors. As a result, the rate and extent of biodegradation can be controlled and can surpass significantly those in land farming

(Riser-Roberts 1998). The composted soil can either be returned to the site of excavation for vegetation restoration or can be used as fill for other sites. Furthermore, the composted soil acts as a slow fertilizer having low levels of inorganic nutrients and high levels of organic nutrients, which may prove beneficial for reclamation purposes (Chaw and Stoklas 2001). Wastes high in HCs (in the form of oil), salt or metals contamination may inhibit microbial activity making the composting process less effective and therefore are not suitable for remediation by composting.

Chaw and Stoklas (2001) conducted a study to evaluate the potential of composting for remediating flare pit soils, which were clay soils with high levels of crude oil contamination. The flare pit soil collected from a site in central Alberta was mixed with manure and wood chips to form an open-air windrow for composting. Aeration was provided by using a self-propelled windrow turner, and the windrow was monitored for other composting parameters such as moisture and temperature for ten months. It was observed that BTEX compounds were removed completely and had high removal rates during the first six months. Extractable HCs ranging from C_5 to C_{10} showed 98.7% removal. However, HCs ranging from C_{11} to C_{60+} achieved only 41% removal, showing a reduction from 94,000 ppm to 55,000 ppm in the last three months of the study. Beaudin et al. (1996) in their study found that co-composting of hydrocarbon contaminated soil with alfalfa and maple leaves proved to be more effective than biopiling. Chaw and Stoklas (2001) determined that the hydrocarbon degrading microorganism population remained high throughout the trial, with most microbial activity occurring within the mesophilic temperature range (35-48°C), and only 10% of the total duration of the trial occurred in thermophilic range (40-65°C). Although a moisture content of about 50-60%

is usually considered optimal for composting, the hydrophobicity or lowered water holding capacity of the flare pit soil only allowed a maximum water holding capacity of the windrow of 35%. The final composted soil, although high in organic matter and nutrients, was found to be more sodic and saline with EC and SAR levels exceeding Alberta Tier I criteria (AEP 1994). However, it was found that despite the high salinity, barley and Timothy plants grew well in the composted soil. Also, it was assumed that the 41% HC reduction was adequate to prevent growth deficiencies in plants (Chaw and Stoklas 2001).

Another lab-scale study by Baheri and Meysami (2002) evaluated the feasibility of fungi bioaugmentation in the composting of a flare pit soil. They evaluated the effect of moisture content and bulking agents on the ability of white rot fungi to degrade HCs. It was found that the total petroleum hydrocarbon (TPH) of 16% present in flare pit soil was reduced by 29% after 98 days. However, fungi application and moisture content did not show any significant effect based on statistical analysis (Baheri and Meysami 2002). On the other hand, April et al. (2000) isolated 64 species of filamentous fungi from five flare pits in Northern and Western Canada and investigated their ability to degrade crude oil. The results indicated that filamentous fungi were capable of degrading the aliphatic fraction of crude oil (nC_{12}-nC_{26}) but no degradation of aromatic or resin fractions were observed.

2.4.2.5 Bioremediation

Madsen (1991) define bioremediation as " a managed or spontaneous process in which biological, especially microbial catalysis acts on pollutant compounds, thereby remedying or eliminating environmental contamination". Microorganisms may assimilate harmful hydrocarbon (HC) contaminants and convert them into biomass, or cell free enzymes may also transform the HC contaminants (Riser-Roberts 1998). Literature shows that bioremediation of PHCs, gasoline, diesel fuel, jet fuel and motor oil can be achieved under certain conditions and at low cost (Riser-Roberts 1998). However, bioremediation is especially effective for remediating low-level residual contamination in conjunction with source removal (FRTR 2002). Hydrocarbon degrading bacteria are commonly found in sub-surface soils, but the natural breakdown of compounds occurs slowly. Bioremediation or bioreclamation enhances the capability of microbes to degrade, transform or attenuate organic or organometallic compounds to non-toxic levels by stimulating the indigenous microbes (biostimulation) or adding developed microbes to the site (bioaugmentation) (FRTR 2002; Riser-Roberts 1998).

The factors controlling the biodegradation of HCs include adequate supply of HC degrading bacteria, availability of sufficient oxygen for cell metabolism (provided by mixing), availability and balance of nutrients and micro-nutrients for optimum bacterial metabolism, optimum levels of moisture, temperature, pH and salinity. In addition, bioremediation treatment often does not require heating, but requires relatively inexpensive inputs, such as nutrients, and usually does not generate residuals requiring additional treatment or disposal. Also, when conducted *in-situ*, it does not require excavation of contaminated media. Compared with other technologies, such as thermal desorption and incineration (which require excavation and heating), thermally enhanced recovery (which requires heating), chemical treatment (which may require relatively expensive chemical reagents), and *in-situ* soil flushing (which may require further management of the flushing water), bioremediation is cost effective (FRTR 2002; Riser-

Roberts 1998). While bioremediation has proved to be effective for treating soil contaminated with medium distillate fuels, it is not effective in removal of heavier HCs present at toxic levels to indigenous organisms (FRTR 2002).

Flare pit soils are believed to contain predominantly heavy PHCs (i.e. n-alkanes ranging from C_{16} to greater than C_{50}). These heavier PHCs have low water solubilities and are often tied strongly to the soil matrix (CCME 2001c), thus reducing their bioavailability and consequently their biodegradation. In addition, the physical and chemical properties of the flare pit soils, the composition of the contaminated crude oil and the composition of the soil micro flora also influence the bioremediation process (Baheri and Meysami 2002). The ability of microbes to degrade hydrocarbons is restricted to certain species, or strains within species (Baheri and Meysami 2002). Moreover, the bioremediation process is difficult to monitor and control, reliable cost and performance data have been difficult to obtain, and the bioremediation process can take anywhere from several months to many years (Riser-Roberts 1998).

A research project involving bioremediation of hydrocarbon contaminated materials common to oil and gas industry was commissioned by the Canadian Association of Petroleum Producers, CAPP (CAPP 1997). The study investigated treatment of crude oil and brine contaminated agricultural topsoil, diesel invert mud, and a flare pit sludge using a full-scale bioreactor. The project focused on the treatment of HCs using microbial oxidation and removal of salts by leaching. Laboratory scale studies determined that a soil water content ranging from 15% to 30%, a temperature ranging from 32°C to 37°C, EC less than 7 dS/m, and sufficient N at initial stages of the treatment were critical to the success of bioremediation of flare pit sludge applied on large-scale

(CAPP 1997). Flare pit material was aggregated by the addition of lime in order to enhance the water movement through the soil and increase nutrient retention. To compensate for the increase in pH by the addition of lime, CO_2 was added to the material. HC degradation rates were enhanced by addition of 2% of previously bioremediated crude oil contaminated topsoil and diesel invert mud. Leaching of flare pit sludge decreased EC from >50 to <20 dS/m, and decreased to about 10 dS/m during the bioremediation process. Other controlled variables during the treatment were temperature, water-content, cultivation, and aeration (CAPP 1997). The study determined that 17.2% HCs were lost in 75 days of bioremediation process using a bioreactor; however, 70% of the total HC pool were lost in the first 40 weeks.

Another study conducted by Amatya et al. (2002) included solid-phase and slurry phase bioremediation for a period of 270 days to investigate the effects of nitrogen, phosphorous, salinity, and incubation temperature on the biodegradation of HCs present in flare pit waste. Slurry based systems showed several advantages, which included reduced mass-transfer limitations by facilitating greater contact between contaminants and microorganism, greater chemical and biological homogeneity, and ensured supply of oxygen, water and nutrients. However, the results obtained from this study concluded that lab-scale slurry treatment does not offer significant advantages by removing mass-transfer limitations in treating flare pit waste. It was found that slurry reactors showed an initial rapid decline in HC concentration, which decreased with time and eventually ceased, leaving recalcitrant compounds. A statistical analysis of the results showed that the primary effect of waste composition was highly significant as the higher clay content resulted in lower biodegradation (Amatya et al. 2002). On the other hand, in solid phase biotreatment, the flare pit soil was treated with different levels of nitrogen, phosphorous and salt, and incubated at three temperatures (20°C, 30°C, 40°C). The results revealed that the highest oil and grease reduction of 34% occurred in soils incubated at 30°C. Soil temperature had more influence on degradation rates than did nitrogen or phosphorous addition. Influence of salinity was also significant as high levels of salinity reduce the osmotic potential of water, thereby reducing the microbial activity and hence the HC degradation rate (Amatya et al. 2002).

2.4.2.6 Thermal Treatment

Thermal treatment processes include all processes that involve heat to destroy, remove or reduce contaminants from an oilfield waste (AEUB 1996b). The contaminated soil is heated under an inert atmosphere to increase the vapour pressure of organic contaminants and convert them into gaseous phase, which separates organics from the soil matrix (Riser-Roberts 1998). The thermal treatment facilities used for treatment of oilfield waste can be either fixed or mobile operational units. Thermal treatment of oilfield waste can be achieved by one of the following processes such as incineration, thermal oxidation, thermal desorption, thermal phase separation, and thermal distillation recovery (AEUB 1996b). AEUB (1996b) strictly forbids the use of thermal treatment for soils contaminated with halogenated organics such as polychlorinated biphenyls (PCBs) unless approved by regulatory agencies. It is known that incineration is the most effective treatment for the complete destruction of organic contaminants. A trial burn with an U.S EPA mobile incinerator achieved 99.9% destruction of carbon tetrachloride, chlorinated benzenes, and PCBs (Riser-Roberts 1998). Organic wastes are usually volatilized and combusted at high temperatures ranging from 850-1200°C. Most of the incineration treatments have been used successfully; however, incineration is generally not considered for the treatment of PHC contaminated soil because of its high cost (FRTR 2002; Riser-Roberts 1998).

Thermal desorption is a non-oxidizing process that uses heat to desorb oil from oily wastes. It can be either low temperature or high temperature desorption. A low-temperature thermal desorption system (90-350°C) may be used to treat light oil contaminated wastes, while a high temperature desorption system (up to 550°C) may be able to achieve lower final oil content for heavy oil contaminated wastes. Decontaminated soil retains its physical properties and ability to support biological activity (FRTR 2002; Riser-Roberts 1998). The heat may be applied either directly or indirectly to the soil, where a barrier is maintained between the burners and contaminated soil (Sherwood 1994). The conventional units known as rotary dryer systems of thermal desorption have been used for treatment of hundreds of sites in U.S contaminated through spills, leaks or accidental discharges. In Alberta, these conventional units, which are directly fired and incorporate an afterburner, have been used to remediate flare pits contaminated with oil and petro-chemical industry waste, and to reclaim the soil associated with these sites (Sherwood 1994). Sherwood (1994) found that metals or salts were not removed from soil on using rotary dryer thermal desorption unit. Moreover, it was determined that the flare pit waste and process pond waste differ from typical wastes, which have been treated through thermal desorption unit. These differences include: the presence of heavier HCs in flare pits with higher boiling point, pockets of material with high concentrations of HCs, high initial moisture contents, and high clay contents due to the lining of the pits with clay. In another project as a part of the same study, remediation of a flare pit at a gas compression and processing site showed that 3-6% oil content in contaminated soil was reduced to 0.9% after homogenization and pretreatment, with final concentration of 29 mg/kg in treated soil. Yet another project (Sherwood 1994) involved remediation of material from 17 small flare pits, which was blended, screened, and fed to the desorption unit. Approximately 2800 tonnes of waste was treated in 9 days of operation, and it was determined that greater than 95% removal efficiencies of standard flare pit HCs could be achieved with high throughput and reliability. Thus, this method can be used readily to treat PHCs up to C_{40}; however, flare pit material and crude oil may contain compounds with carbon numbers of C_{70} and above (Sherwood 1994).

Catalan et al. (1998) investigated the treatment of flare pit soil using a low temperature thermal treatment process in which the contaminated soil was oxidized with air at temperatures ranging from 150-170°C for three weeks, as a result of which PHCs were converted into inert coke. The oxidized soil was black, with no smell, and was extremely consolidated. It was determined that the extractable PHCs level was reduced to less than 0.1% by mass, and that the toxicity associated with the PHCs was eliminated. However, salinity of the treated soil remained the same, showing that it was not reduced during the coking process. The soil can further be leached by 'waterflooding' to remove the salts (Catalan et al. 1998). Moreover, pH value of 3.6 of the oxidized soil suggested that acidic compounds were produced during the coking process, through the hydrolysis of small highly charged metal cations. Thus, low temperature oxidation was found effective in eliminating hydrocarbon toxicity from the contaminated flare pit soil, but created an acidic soil with a potentially high salt content.

2.5 SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction (SFE) is a promising new technology that is being investigated for remediation of contaminated soils. SFE is a solvent extraction process that uses a supercritical fluid (SCF) as the solvent. A compound is said to be in its supercritical state when it is heated and compressed above its critical temperature (T_c) and pressure (P_c). The pressure temperature (P-T) diagram showing the supercritical fluid region is shown in Figure 2.1. As the temperature and pressure increase along the gas-liquid co-existence curve (Figure 2.1), the thermal expansion of the liquid makes it less dense, while the gas becomes denser due to pressure rise (Clifford 1999), eventually leading to the identical densities of the two phases. This point where the distinction between the liquid and gaseous phase disappear leading to identical densities is known as the critical point (Cr), and the region above this critical temperature (Tc) and critical pressure (Pc) is called the supercritical fluid region. Thus, in the supercritical state (or supercritical fluid region as shown in Figure 2.1), the substance exists as a single fluid phase with properties intermediate between those of liquids and gases (Bright and McNally 1992; Hedrick et al. 1992; Vanwasen et al. 1980). The densities of SCFs are liquid-like while the diffusivities and viscosities are gas-like (McHugh and Krukonis 1994). Supercritical solvents are regarded as effective solvents as they enhance the solubilities of high molecular weight organic molecules (Tomasko et al. 1995). A simple adjustment of temperature and pressure allows fine-tuning of the solvating power of the SCF. This adjustment allows SFE the advantage of selectivity for extraction of different compounds (Phelps 1996; Tomasko et al. 1995; Akgerman 1993). In addition to this solubility enhancement, SCFs have high diffusivities and low viscosities, properties that lead to advantageous mass transfer characteristics (Bowadt and Hawthorne 1995). SCFs have zero surface tension, which allows easy penetration into most matrices including soil (Akgerman 1993; Erkey 1993).

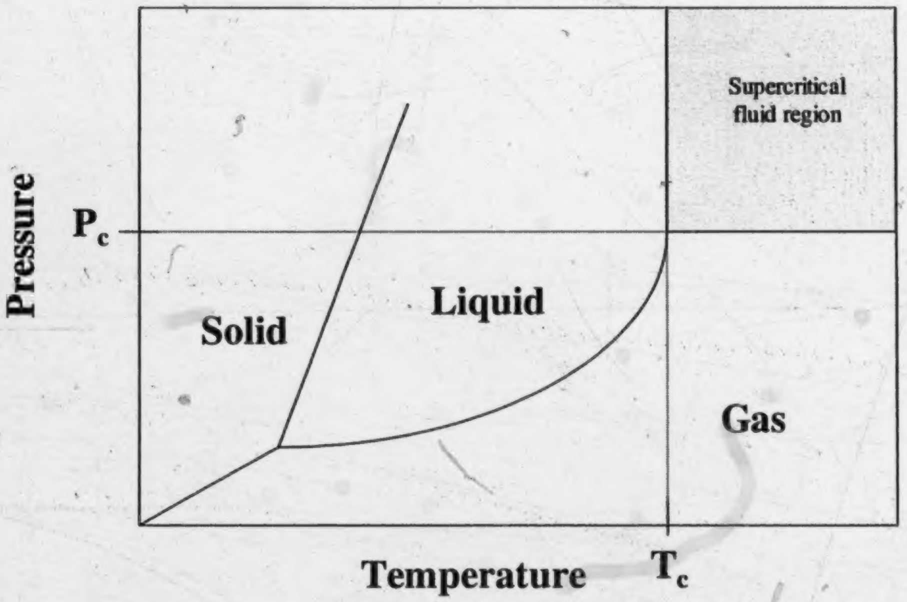


Figure 2.1: Pressure-Temperature phase diagram of carbon dioxide (adapted from Laitinen et al. 1994)

Most SFE processes use CO_2 as the SCF since CO_2 is non-toxic, non-flammable, chemically inert, and it has a moderate and relatively technically achievable critical point of 31°C and 7.38 MPa. CO_2 is available in high purity at relatively low cost, as it can be obtained in large quantities as a by-product of fermentation, combustion, and ammonia synthesis (Clifford 1999). CO_2 can be easily removed from the soil matrix and can easily be separated from the extracted contaminants leaving the soil structure and the soil nutrients relatively intact (Laitinen et al. 1994). CO_2 is non-polar and hence is best suited for the extraction of non-polar organic compounds including hydrocarbons and oils (Chester et al. 1998; Bowadt and Hawthorne 1995; Laitinen et al. 1994). However, addition of modifiers such as methanol and water may enhance the polarity of supercritical carbon dioxide (SC CO_2) (Phelps 1996). Other modifiers may be added to change the solvent character of SC CO_2 to suit the desired application. For example, methanol is added to increase polarity, aliphatic hydrocarbons are added to decrease polarity, toluene may be added to impart aromaticity, and tributyl phosphate may be added to enhance the solvation of metal complexes (Clifford 1999). Other fluids, such as N_2O, freon, argon, propane and SF_6 have been used as SCFs in various applications but issues such as disposal, toxic emissions, and flammability limit their use (Bowadt and Hawthorne 1995).

Generally, during supercritical fluid extraction of contaminated soil, the soil matrix to be cleaned is placed in a closed vessel where it is exposed to a supercritical fluid (SCF e.g. SC CO_2). Once the equilibrium is reached between the contaminant and the supercritical solvent, the SCF containing the contaminant is allowed to flow out of the reactor through a depressurization device. As the SC CO_2 depressurizes with the termination of the supercritical conditions, the solubility of the contaminant solubilized in the supercritical solvent decreases and the contaminant separates out of the solution and is collected into solvent traps. The CO_2 can be recycled, reused or vented (lab-scale) in the SFE process. The SCF containing the contaminant may be depressurized to atmospheric conditions to allow complete separation of the contaminant from SCF.

In their supercritical state, SCFs are extremely sensitive to small changes in temperature and pressure such that a solute may be extracted from a matrix at one set of conditions and completely separated from the solvent in a downstream operation at slightly different conditions (Tomasko et al. 1995). Pressure and temperature are the two most important physical parameters determining the supercritical extraction process. Together they define the density of SCF, the highest of which is achieved at high pressures and at temperatures near the critical temperature of the SCF (for SC CO_2, the critical temperature is 31°C).

The contaminant's solubility in SCF depends on the volatility of the solute and the solvating effect (density dependent) of the SCF (Bowadt and Hawthorne 1995). It is believed that increasing solubility favors the partitioning of PHC molecules from internal matrix sites into the bulk SCF (Li Jun et al. 2003). For a volatile solute, the extraction efficiency is believed to increase with an increase in temperature. However, a decrease in extraction efficiency will be observed due to a decrease in density if the vapor pressure of the solute does not increase with an increase in temperature (Laitinen et al. 1994).

SFE has several distinct advantages over the conventional liquid extraction methods used in soil remediation. Most notably, the contaminant is removed from the solvent in a concentrated form via a change in pressure and temperature conditions, and can be completely separated upon expansion to atmospheric pressure. Some of the other advantages are the qualitative recovery of the contaminants within 15-60min., reduction in solvent usage and waste generation, elimination of solvent residues in the soil, and no generation of solvent waste streams that may require post-treatment for disposal (Smart et al. 1998; Akgerman 1993; David et al. 1992). Moreover, the extraction solvent (e.g. SC CO_2) used in the SFE process can be easily recovered using a recompression unit and recycled to be used in subsequent extraction runs. Conventional extraction methods used for the extraction of contaminants from soil are time consuming; require large quantity of pure and expensive solvents, and produces large amount of waste solvents. SFE has shown to be an attractive alternative to solvent extraction due to the better mass transfer and solubility characteristics of SC CO_2, shorter extraction times and ease of extract separation.

2.5.1 Current status of SFE and its role in soil remediation

U.S EPA promotes pollution prevention through source reduction that are useful to petrochemical industries. SFE thus has been promoted as an industrial scale extraction technique (Rudzinski and Aminabhavi 2000). SFE has been used on a commercial scale in the food industry for decaffeinating of coffee (Ramalakshmi and Raghavan 1999; Peker et al. 1992; Udayasankar et al. 1986), and for the extraction of vitamins, edible oils, hops and spices from food and agricultural products (Caredda et al. 2002; Eller and King 2000; Brunner 1998; Illes et al. 1997; Peusch et al. 1997; Valcarcel and Tena 1997; Miller et al. 1995). SFE is beginning to appear in other industries such as in the spray application of varnishes and paints (Donohue et al. 1996), in the cleaning of electronic parts and in the polymer industry (Howdle 2002; Kazarian 2002; Gamse and Marr 2001; Tomasko et al. 1995).

Various studies have investigated the use of SFE for removing toxic organic compounds from contaminated soils. SFE has been used to recover hydrocarbons, poly-aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs and dioxins), phenols, chlorinated phenols, metals, and many pesticides and herbicides from contaminated soil, sediment and other environmental matrices (Liang and Tilotta 2003; Chen et al. 1997; Lee and Gongaware 1997; Low and Duffy 1995; Tomasko et al. 1995; Laitinen et al. 1994; Eckert-Tilotta et al. 1993; Lopez Avila et al. 1993; Laintz et al. 1992; Hess et al. 1991; McNair and Frazier 1991; Dooley et al. 1990; Brady et al. 1987). A recent comparative study by Hawthorne and Grabanski (2000) on 1 year and ½ year bioremediated soils, proved SFE to be an excellent, fast, and better treatment technology as compared to bioremediation. The results determined that the amount of PAHs extracted from the contaminated soils were higher than those obtained after 1 year of bioremediation. The extraction of the contaminants from soil using SFE strongly depends on the type of soil, its moisture content, the nature and type of contaminant being removed from the soil, addition of modifier/co-solvent and changes in temperature and pressure conditions. The following sections describe the effect of soil type and other factors on the extraction of organic contaminants from the soil using supercritical carbon dioxide (SC CO_2) followed by brief review on SFE of organic contaminants from soil matrices.

2.5.1.1 Effect of soil type

The properties that affect the SFE process include the type of soil matrix, its physical and chemical properties (e.g. porosity, pore size, particle size), the type of contaminant and its extent of adsorption, and the water content (Tomasko et al. 1995). Organic contaminants may be difficult to remove from soils rich in organic material due to the strong bond formation between the organic pollutants and the organic matter present in the soil. Clays that have high Al^{3+} and Fe^{3+} contents may absorb organic acids and bases and highly polar non-ionics (Dooley et al. 1987).

The extraction from a porous matrix depends on the solid-fluid interface, the rate of diffusion/desorption of the analyte from the pores, and consequently on the diffusion of the analyte from the external surface of the particle to the bulk fluid (Bowadt and Hawthorne 1995; Tomasko et al. 1995). Soil with a smaller particle size will have larger surface area per unit volume, and thus will have a stronger affinity for the contaminants. This affinity will result in a reduction in the solubility of the contaminant in SCF and thus, a reduction in extraction efficiency of the contaminant. Its reduction in solubility may also be due to the mass transfer limitations (Bowadt and Hawthorne 1995; Tomasko et al. 1995). Cocero et al. (2000) studied the effect of particle size on the PHC extraction from the soil. He concluded that better extraction is obtained from soil with bigger particle size because for aged soil, pollutants are more strongly adsorbed onto soil and the effect of particle size is not as important as bond forces. Another study on six different soils on the distribution of phenol between adsorbed and fluid phases concluded that surface area is a primary factor in determining distributions, as distribution coefficients steadily decreased with an increase in surface area (Hess et al. 1991). Cai (1990) reported lower extraction efficiencies of PCBs and pesticides from clays because of small particle size and high adsorption capacity; only a small increase in extraction efficiency was observed when particle size was increased. In another study by Burk and Kruus (1990), particle size had no effect on the extent or rate of extraction of fluoroanthene from sand. The heterogeneous nature of soil affects the affinity of the contaminant to the soil matrix.

Most soils are made up of a complex mixture of sand, silt, clay, organic matter and various debris, the composition of which, largely influences the extraction of PHCs (Eckert-Tilotta et al. 1993). It is believed that of the soil types, clay has the strongest affinity for organic contaminants followed by loam and silt (Eckert-Tilotta et al. 1993). Moisture content in soil may affect the rate of extraction by influencing sorption of pollutants in the soil, and by influencing the equilibrium distribution of the solute between solid and fluid phases (Laitinen et al. 1994). Variability in water content affects the elasticity and the degree of compaction of the soil particles (Laitinen et al. 1994). Change in water content and pressure may affect the soil permeability and hence the extractability of the contaminant (Hawari et al. 1997). On the contrary, it is difficult for wet soils (having >40% water) to undergo compaction as most of the air in the soil voids is now replaced by water, thus restricting CO_2 to reach inner regions of the matrix and trap the contaminants (Hawari et al. 1997). The presence of water in bound and unbound forms greatly influences extraction of PHCs from soils (Low and Duffy 1995). Bound water is mainly associated with the clay component of the soil, which causes the soil matrix to swell and enable penetration of analytes into the intracrystalline layer of the clay structure (Low and Duffy 1995). For example, Lopez-Avila and Dodhiwala (1990) found that adding upto 10% water improved recovery of the PAHs. On the other hand, Brady et al. (1987) showed a much slower removal of PCBs and DDT from soil containing 20% water (wt.%) than from dry soil, although final concentration on the soil was approximately the same (60-70% removal). Similarly, Liu (1991) demonstrated a significant decrease in extraction efficiency with an increase in soil moisture content. Thus, the role of most of the properties of the soil matrix in SFE process is still unclear and is a current area of further research.

2.5.1.2 Removal of Petroleum Hydrocarbons (PHCs).

Contamination of soil by PHCs poses a serious threat to the environment and is of prime concern these days. Contamination may result from leaks or spills from pipeline or underground storage tanks, accidents, railroad cars, and disposal of petroleum and refinery waste, etc. PHCs are extremely complex class of compounds with wide range of physical and chemical properties (Morselli et al. 1999; Potter et al. 1993). The binding and removal of PHCs from soil is largely influenced by the textural property of soil and by the amount of organic content and moisture present in the soil (Low and Duffy 1995). The degree of differences in the solubilities and sorption of PHCs in the SCF and on the soil particles, the moisture content, and the presence of other organic constituents in the soil represent major extraction problems (Morselli et al. 1999; Hawari et al. 1995). U.S Environmental protection Agency in 1992 approved SFE method in lieu of other conventional methods for the extraction of total petroleum hydrocarbons from contaminated soils, which have been used until then (Morselli et al. 1999). Conventional solvent extraction methods such as sonication and soxhlet extraction used for the extraction of PHCs from the soil are limited by the waste streams produced and by the time and the quantity of solvents consumed (Morselli et al. 1999; Low and Duffy 1995). Thus, focus had shifted to develop fast, cost effective, alternative techniques for the remediation of PHC contaminated soils.

Many studies are being conducted to evaluate the efficiency of extraction of diesel range and heavier PHCs from contaminated soils using SFE. However, most of the SFE studies have been conducted on the extraction of PHCs in the range of C_6 to C_{36} n-alkanes using spiked soils, very few studies have been published related to the SFE of heavier PHCs and from real world contaminated soil samples (Liang and Tilotta 2003; Hawari et al. 1997; Hawari et al. 1995; Hwang et al. 1995). Spiked analytes tend to stay on the surface of the soil matrices and have little time to migrate to strong binding sites, whereas native pollutants/contaminants that are in contact with soil matrices for years tend to bind strongly to the matrix sites. Thus, spiked analytes are extracted rapidly as compared to the native contaminants from old-weathered contaminated soils (Bowadt and Hawthorne 1995). Hence, results from recently spiked soils cannot be used to predict the behaviour of aged soil samples specially the heterogeneous environmental samples (Bjorklund et al. 2000).

The quantitative recovery of PHCs from contaminated soil is dependent on the type of soil, type of contaminant, the interaction between the soil and the contaminant, the supercritical fluid, and the mode of extraction (Rudzinski and Aminabhavi 2000; Low and Duffy 1995). It has been suggested that in cases where extraction is controlled by solubility, pseudo-dynamic extractions i.e. a static step followed by dynamic phase may be useful (Rudzinski and Aminabhavi 2000; Low and Duffy 1995). Lee and Gongaware (1997) determined that more than 95% of diesel fuel could be recovered from contaminated soil. Pressures ranging from 15.2 MPa to 40.5 MPa and temperatures ranging from 40°C to 150°C are considered optimal for SFE of petroleum hydrocarbons (n-alkanes ranging from C_6 to greater than C_{34}) from contaminated soils (Low and Duffy

1995; Eckert-Tilotta et al. 1993; Lopez-Avila et al. 1992). For example, Eckert-Tilotta (1993) reported 57%, 79% and 63% recovery of hydrocarbons (greater than C27) at 40.5 MPa and 65°C, 40 MPa and 150°C, and 68 MPa and 65°C, respectively. This showed that an increase in temperature from 65°C to 150°C was more effective than an increase in pressure, even though the density at 68 MPa and 65°C (0.98 g/mL) is higher than at 40 MPa and 150°C (0.61 g/mL). On the other hand, at similar density of 0.65 g/mL but achieved at 80°C and 22.7 MPa, Morselli (1999) obtained 70-100% recoveries of saturated and aromatic fractions from crude oil in clayey-sandy soil. Lopez-Avila et al. (1992) reported complete recovery of C_{20} to C_{38} hydrocarbons mixtures at 34.5 MPa and 80°C. Low and Duffy (1995) reported 99% removal of diesel from contaminated soils at 15 MPa and 40°C and 98.6% removal of C_{36} at 34.5 MPa and 80°C.

An interlaboratory study was conducted to investigate the accuracy and precision of EPA Methods 3560 and 8440 for the extraction of PHCs from four solid matrices contaminated with PHCs ranging from 614 mg/kg to 32600 mg/kg using SC CO_2 at 34 MPa and 80°C for 30 minutes (Lopez Avila et al. 1993). Its results indicated an overall accuracy of 83% with mean recoveries of PHCs for each of the four solid matrices ranging from 78% and 107% (Lopez Avila et al. 1993). Eckert-Tilotta (1993) also quantitatively extracted total petroleum hydrocarbons (TPH) at 40 MPa and 150°C from real world fuel spill samples containing heavy fuel oil, diesel fuel, light crude oil, gasoline or kerosene, and compared the results to soxhlet extraction. It was found that SFE yielded higher TPH quantities as compared to soxhlet extraction (134% SFE vs soxhlet), and that water seemed to affect the SFE recovery of PHCs and not via soxhlet. However, SFE of PHCs functions well at 20% water content, where a lower moisture content tends to increase the PHCs recovery (Hawari et al. 1995). Liang and Tilotta (2003) also obtained agreeable results for extraction of TPH from real world soil samples collected from adjacent to a fuel tank and from near rail road tracks, when compared with soxhlet extraction. On the contrary, Hawari et al. (1997) in their study for extraction of PHCs from 10-15 years old contaminated soils suggested soxhlet seems to produce more realistic data than SFE on real aged soils. It was determined that variations as high as 80% in the recovery of PHCs from aged soils can be observed by simply changing the type and amount of drying agent.

2.5.1.3 Removal of Polyaromatic hydrocarbons (PAHs)

PAHs are neutral, non-polar organic molecules that are produced during incomplete combustion of fossil fuels and in the processing of petroleum products. They are composed of two or more benzene rings and represent one of the major constituents of creosote oils used as wood preserving agents.

SFE with CO_2 has been known to completely recover low molecular weight PAHs from landfill soil (McNair and Frazier 1991), coal tar contaminated soil (Wright et al. 1989) railroad bed soil, and petroleum waste sludge (Hawthorne et al. 1992). Lopez-Avila et al. (1993) extracted 16 PAHs from various soils with average recoveries of 57%, 89% and 96% from urban dust, coal fly ash and coal, respectively. The recoveries of different PAHs were found to be in the range of 31% to 96% (Lopez Avila et al. 1993; Hawthorne et al. 1992; McNair and Frazier 1991). Wenclawiak et al. (1992) found that the recovery of 3-, 4-, 5- ring PAHs by SFE were comparable to or higher than that achieved by Soxhlet extraction with toluene. Increasing molecular size and decreasing vapor pressure decreases the recovery of PAHs (Hawthorne et al. 1992; Wright et al. 1989). Hawthorne et al. (2000) obtained similar PAH recoveries with SFE when compared to the results obtained by Soxhlet extraction, pressurized liquid extraction (PLE), and subcritical water extraction. However, discrepancies in the recovery of PAHs from PAH contaminated soils may also be due to the effect of storage time. A recent study investigating the stability of PAHs in the historically contaminated soils in the cold storage at 4°C and –20°C suggested that significant losses of lighter PAHs occur during storage/sample holding time of 8-10 months (at 4°C), and quantitative recovery of heavier PAHs were observed (Rost et al. 2002). Rost et al. (2002) indicated significant losses of 3-5 ringed PAHs over a holding time of about 2 weeks; however, freezing of the samples at –20°C or addition of a biocide such as sodium azide as a means of preservation was suggested for stability of the samples expected to have microbial degradation of compounds.

PAH recoveries were favored by higher pressures of up to 35 MPa (Langenfeld et al. 1993; Burk and Kruus 1990; Yu et al. 1990). A significant increase in temperature from 50°C to 200°C may have little or no effect depending on the nature of soil and interaction between the soil and the contaminant (Langenfeld et al. 1993). Other studies found that increasing the temperature to 200°C compared to lower temperatures increased the extraction of PAHs from soil, bituminous fly ash, marine sediments, urban air particulate and diesel soot. Addition of water as an entrainer in a continuous or discontinuous manner strongly increases the desorption of PAHs from contaminated soil and spiked silt (Schleussinger et al. 1996; Kothandaraman et al. 1992; Andrews et al. 1990). The soil absorbs the water and releases PAHs from the adsorbed sites (Laitinen et al. 1994). Water decreases the extraction rate due to an additional phase formation; however, it increases the accessibility of the contaminant, allowing a faster transport out of the soil (Schleussinger et al. 1996). Addition of water upto 10wt% increases the extraction recoveries (Lopez-Avila and Dodhiwala 1990), but addition of more water causes a decrease in recovery (Akgerman 1993). Also, addition of methanol as a modifier to the SC CO_2 has shown to increase PAH recoveries to higher than 90% (Monserrate and Olesik 1997; Levy et al. 1992; Lopez-Avila and Dodhiwala 1990; Yu et al. 1990).

SFE process (at 40 MPa and 140°C) developed on pilot scale for the removal of PAHs from soil obtained from former industrial sites reduced the PAH levels in soil to less than 1 mg/kg (Schulz and SchleuBinger 1995). A recent comparative study by Hawthorne and Grabanski (2000) on the SFE of PAHs from a manufactured gas plant site proved SFE to be an excellent fast treatment technology for real world contaminated soils. Hawthorne and Grabanski (2000) found that one-hour of SFE of the untreated sample at the conditions of 12 MPa and 50°C gave good quantitative agreement with the removals achieved after 1 year of bioremediation. Hawthorne and Grabanski (2000) reported a reduction of PAHs from a concentration of 6860 mg/kg in untreated soil to 2360 mg/kg in SFE treated soil. Treatment by SFE yielded better results than those achieved after one year of bioremediation of the same PAH contaminated soil.

2.6 SUMMARY

Even though a large number of options are available for treatment of oil field wastes, only a few are being practised currently as treatment options for flare pit soils.

The variability in the characteristics of the flare pit soils has limited the number of treatment options mainly to excavation followed by land treatment, bioremediation, composting or thermal treatment. The literature suggests that these treatment options have been used successfully to treat flare pit sites contaminated with lighter PHCs although still limited by heavier recalcitrant PHCs, which are difficult to biodegrade.

Supercritical fluid extraction is a promising new technology that may be used to remediate flare pit sites contaminated with heavy and biorecalcitrant PHCs. The SCF has properties intermediate between those of a liquid and a gas, and has zero surface tension. These properties prove it to be a valid alternative, which provides better mass transfer properties of SCFs, shorter extraction times and ease of extract separation. Supercritical solvents are regarded as effective solvents as they enhance the solubilities of high molecular weight organic molecules. The solubility of the contaminant in SCF, and the eventual separation of the SCF from the contaminant can be achieved easily by manipulating the extraction conditions of temperature and pressure. Most of the extraction performances are density dependent, i.e. the extraction efficiency of heavy HCs increase with an increase in density, which is pressure dependent (Hwang et al. 1995). The performance also depends on the differences in the volatilities and the intermolecular forces between the solutes and the SFE solvent. Carbon dioxide was used as the supercritical solvent in this research, due to its favourable characteristics of being environmentally friendly, inflammable, inexpensive, widely available, and no additional residue left on the treated soil after extraction.

CHAPTER 3. MATERIALS AND METHODS

The following chapter outlines the materials and methods used to evaluate the extraction of petroleum hydrocarbons (PHCs) from flare pit soils using supercritical carbon dioxide.

3.1 MATERIALS

The following sections present the chemicals and other materials used for this research.

3.1.1 Flare pit soils

Two flare pit soils were investigated in this research that are illustrated in Figure 3.1. Both soils were collected from two sites located in the province of Alberta (Canada). FP 1 was obtained from a site near Redwater, northeast of Edmonton, Alberta on August 8, 2002. This flare pit site is approximately 54 years old and covers an area of 600m^2 (20m×30m) and a depth of approximately 1.5m. Contaminated soil was collected at a depth of approximately 1.25m. Clean soil was also collected at a distance of few meters outside the contaminated site. Both the contaminated soil and clean soil were transported to the Department of Civil and Environmental Engineering at the University of Alberta where they were stored in the cold room at 4°C. Both soils were homogenized by first removing rocks and agglomerated soil and then by sieving through a 2 mm sieve. The homogenized, sieved soils were then mixed thoroughly and placed in sealed containers for storage at 4°C.

FP 2 was obtained from a second site near Devon, southwest of Edmonton, Alberta on January 29, 2003. This flare pit site is approximately 20 m in diameter covering a circular area of approximately 314 m^2. No information on the age of the site was available. Contaminated soil was collected at a depth of 1.5 to 2 m and transported to the Department of Civil and Environmental Engineering at University of Alberta where it was stored in the cold room at 4°C. The soil was homogenized and sieved using the same procedure as for FP 1 and was placed in sealed containers for storage at 4°C.

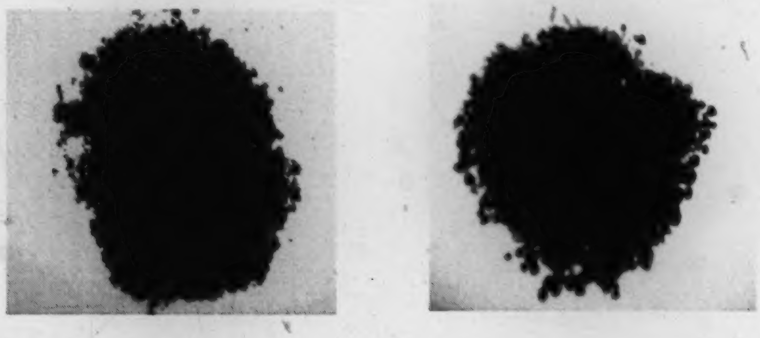


Figure 3.1: **FP 1 (left) and FP 2 (right) used in the research**

The flare pit soil 1 (herein referred to as FP 1) was dark granular sand where the sand particles were agglomerated together due to the PHCs present in the soil. Flare pit soil 2 (herein referred as FP 2) was a darker (dark brown-black) coloured loam. Both have a strong characteristic petroleum hydrocarbon odour. Figure 3.1 shows the picture of contaminated FP 1 and FP 2. Sub-samples from these soils were kept in glass sample jars with minimal headspace. The jars were Teflon™-taped and stored at 4°C in a refrigerator.

Two sub-samples (one from each soil) were sent for characterization to the Department of Earth and Atmospheric Sciences at the University of Alberta. Table 3.1 shows the physical and chemical properties of FP 1, FP 2 and the clean flare pit soil. Based on the depth of the collection of the two soils, FP 1 is a surface soil (collected at 1.25 m depth <1.5 m), and FP 2 is a sub-soil (collected at >1.5 m depth). Samples of FP 1 and FP 2 were also sent to commercial laboratories for PHC analysis. In this research only three fractions of PHCs (F2, F3, and F4) were being investigated. This was because the flare pit soil under investigation was 54 years old and weathered flare pit soil that had been exposed to the open environment for many years. As a result of exposure to air, it was assumed that the lighter HCs (F1 fraction) must have been volatilized.

For quality control, two spiked samples (clean sand spiked with weathered diesel oil – known amount of diesel oil kept in open beaker for three months) were also sent along for the same PHC analysis as were the samples. The results of the PHC analysis for FP 1, 2 and clean flare pit soil are presented in Table 3.1. According to the data shown in Table 3.1, the electrical conductivity (EC) for FP 2 exceeds the Canadian Soil Quality Guidelines (CCME 2001b). For both FP 1 and FP 2, the PHC content exceeds the required soil quality criteria as per *Canada Wide Standards for Petroleum Hydrocarbons in Soil* in an industrial area (CCME 2001a). The results of the particle size analysis provided in Table 3.1 shows the textural class of both soils indicating that FP 1 is coarse grained sandy soil and FP 2 is fine textured loam in nature.

Table 3.1: Characterization of Flare pit soils

PARAMETER	FP 1	FP 2	CLEAN FLARE PIT SOIL
Particle Size Distribution			
Sand (>50μm) (%w)	95.57	41.94	93.91
Silt (2-50μm) (%w)	0.17	43.94	2.90
Clay (<50μm) (%w)	4.27	14.12	3.19
Soil Type	sand	loam	sand
Electrical Conductivity (EC) (dS/m)	3.98	8.77	0.179
Sodium Adsorption Ratio (SAR)	3.90	11.30	1.62
Petroleum Hydrocarbon Content (PHC)*			
F2 (C_{10}-C_{16}) mg/kg	3300	19000	<5
F3 (C_{16}-C_{34}) mg/kg	17000	64000	<5
F4 (C_{34}-C_{50}) mg/kg	12000	34000	<5

*(CCME 2001b)

3.1.2 Motor Oil and Weathered Diesel Oil

The amount of petroleum hydrocarbon fractions present in the untreated and treated flare pit soils were analyzed by a gas chromatograph/flame ionization detector (GC/FID). This chromatographic analysis required the use of motor oil and weathered diesel oil. The SAE 10W-30 motor oil (purchased from Canadian Tire) was used to check the calibration and to prepare spiked samples of clean sand for analytical method quality control. Small amount of diesel oil was placed in a beaker exposed to air in the lab for three months. This weathered diesel oil was used to spike sand at a desired concentration so as to mimic the 54 year old weathered flare pit soil. SAE 10W-30 motor oil was kept in glass sample jars with minimal headspace, Teflon^{TM}-taped and stored below 4°C in a refrigerator.

3.1.3 Sand

For quality assurance of the GC/FID analyses, clean sand spiked with weathered diesel oil at known concentrations was analyzed. The sand was Sil 1 (60-100) of effective size 0.15 mm purchased from Sil Silica Inc. (Edmonton, AB). It was obtained by the Geotechnical Group in the Department of Civil and Environmental Engineering at the University of Alberta

3.1.4 Chemicals

The extractions were carried out using '4.51 Supercritical grade' carbon dioxide cylinders obtained from Praxair (Edmonton, Alberta). Toluene (Optima grade, Fisher Scientific, Nepean, Ontario) was used as the extraction solvent in solvent extraction process (soxhlet extraction) and to clean the extraction vessel after extractions. Toluene was also used as the solvent for preparation of calibration standards for n-alkanes (C_{10}, C_{16}, C_{34}, C_{50}) for retention time determination, and for motor oil standards for GC calibration check. Also, toluene was used in the solvent trap vials during extractions to collect any petroleum hydrocarbons that were not removed by the first glass bead trap (see Section 3.2.1). A 50:50 mixture of acetone (GC Resolv, Fisher Scientific, Nepean, Ontario), and hexane (GC Resolv, Fisher Scientific, Nepean, Ontario) was used as the liquid solvent during soxhlet extraction process (see Section 3.2.3.1). Granular anhydrous sodium sulphate (Chemistry store, University of Alberta) was used to remove water and any impurities or polar compounds present in the soxhlet-extracted sample.

Decane (C_{10}, 99+%, Acros Organics, New Jersey), hexadecane (C_{16}, 99%, Acros Organics, New Jersey), tetratriacontane (C_{34}, 98%, Sigma-Aldrich Canada Ltd., Ontario), and pentacontane (C_{50}, Sigma-Aldrich Canada Ltd., Ontario) were used for standards preparation for alkane retention time determinations and calibration of GC/FID as described in Section 3.2.3.2.

3.1.5 Extraction vessel

The vessel used for the SFE extractions is a 300 mL stainless steel bolted enclosure vessel supplied by Autoclave Engineers (Division of Snap-Tite Inc., Erie, Pennsylvania). The vessel, the vessel parts and the vessel mounted on its stand are illustrated in Figures 3.2 to 3.5. The vessel has a diameter enclosure of 1.81" (45.9mm). An insulated jacket installed to recirculate water at desired temperature surrounds the body of stainless steel vessel. Figure 3.2 depicts the configuration of the vessel cover as presented by Autoclave Engineers (2002). There are four 1/8" NPT openings (C, B, J, E) on the cover diagonally opposite each other. The vessel cover along with the socket head cap screws is permanently attached to the bolted system. The configuration is detailed by Autoclave Engineers (2002). Figure 3.3 shows the simpler schematic of the vessel cover with only the openings that were used during the extraction runs. Openings ‘J’ and ‘C’ were used as the inlet and outlet for SC CO_2, respectively. Opening ‘G’ served as the opening for the thermistor probe (OD YSI 406 thermistor probe (manufactured by Electrical Group at the University of Alberta). At the centre of the cover (opening ‘K’), a MagneDrive^{TM} mixer (with a maximum operating speed of 3300 rpm) is installed. The manufacturer’s suggestions were followed to assemble the vessel (AutoclaveEngineers 2002). A Teflon O-ring was placed between the vessel and the cover when closing the vessel.

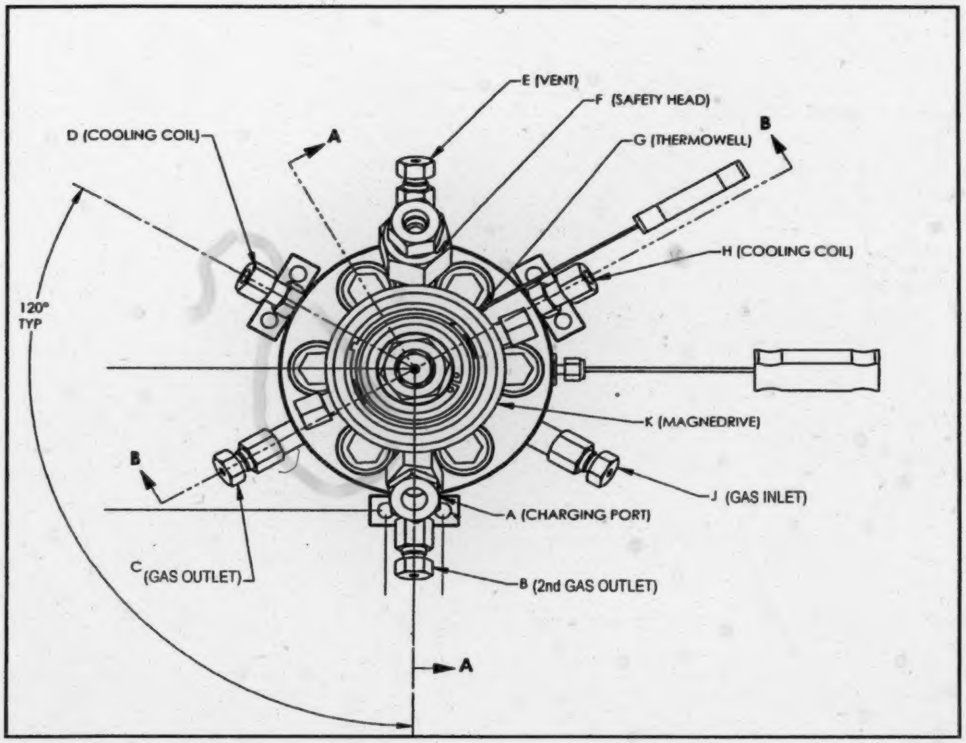


Figure 3.2: **Pressure vessel cover (diagram supplied by Autoclave Engineers)**

1/16" stainless steel tubing (chromatography grade, Fisher Scientific, Nepean, Ontario) was used for connections throughout the assembly (from the valves to inlet to outlet assembly). Two 1/16" to 1/8" stainless steel male connectors (Zimco Inc., Calgary, Alberta) were placed at the inlet and outlet positions that allowed the 1/16" outside diameter, 0.05 mm inside diameter (ID) stainless steel tubing to extend into the openings. Although, only outlet 'C' was used in this research work to carry out extractions, both outlets 'C' and 'B' on the cover were plugged with glass wool (Supelco, Bellefonte, Pennsylvania) to prevent entrainment of soil particles with the supercritical fluid during extractions. This ensured that process valves and tubing downstream of the vessel were protected from plugging with entrained soil particles and fines.

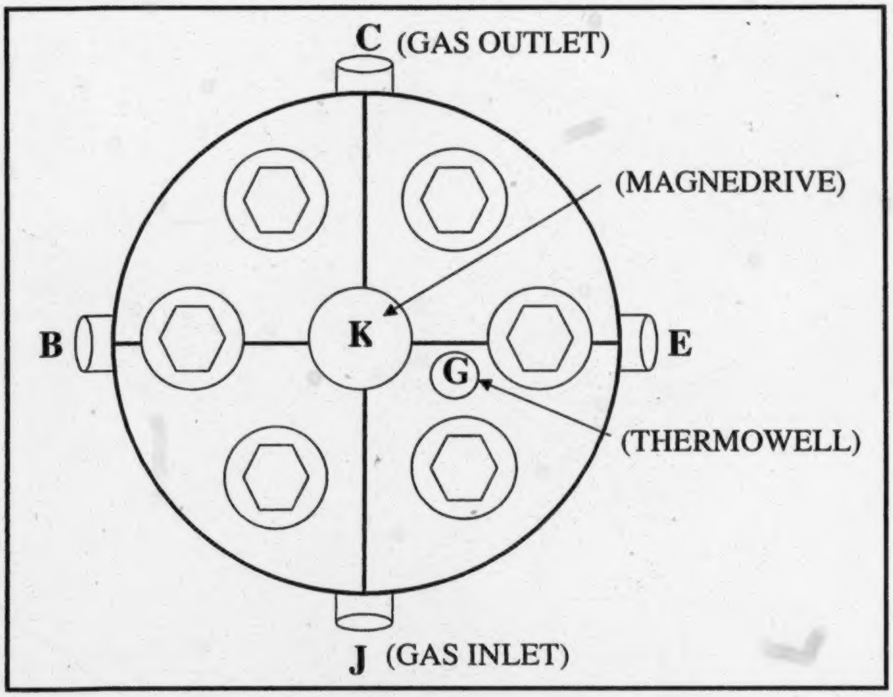
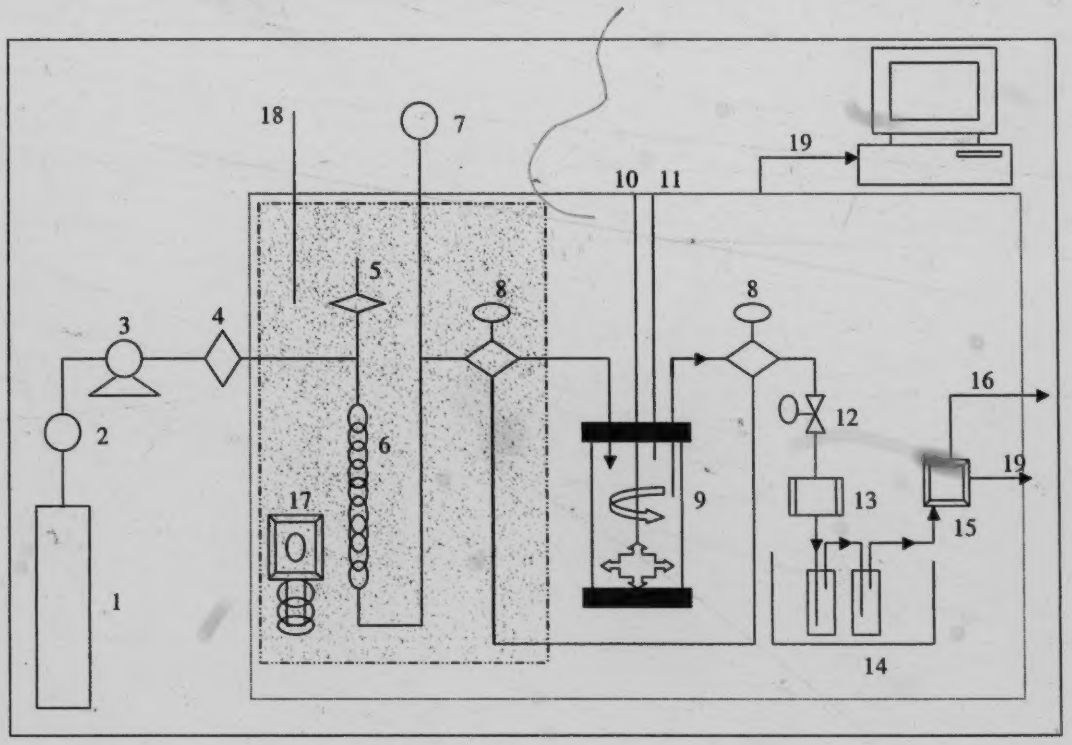


Figure 3.3: **Schematic of pressure vessel cover**

The vessel was carefully placed onto the fixed cover so that the opening for the screws on the cover and the vessel body were properly aligned. The bolts' threading and the bolt openings in the vessel were frequently lubricated with Jet-Lube MP-50 Moly-Paste (Jet-Lube of Canada Ltd., Edmonton, Alberta). The bolts were threaded down firmly into the vessel body using an Allen wrench. The screws were then tightened in the following sequence using a torque wrench (ATD Tools Inc., Edmonton, Alberta): (i) tighten diagonally opposite bolts at a torque of 25 ft-lb_f so as to align the vessel properly, (ii) repeat the tightening pattern at a torque of 35 ft-lb_f, and then 43 ft-lb_f. This tightening pattern prevents leaks when running at high pressures.

3.1.6 SC CO_2 Extraction Apparatus

Figures 3.4 and 3.5 shows a schematic and a photograph of the SFE system used in this research. Table 3.2 describes the main components, suppliers and applicable information on the SFE system. Supercritical grade CO_2 (Praxair, Edmonton, Alberta) supplied by a cylinder pressure of around 5.86 MPa was used in the experiments. The CO_2 from the cylinder passed through a filter and was pressurized using an ISCO 500D continuous flow syringe pump. For efficient functioning, the pump heads were cooled to 7.5°C using a circulating refrigerated water bath and temperature control jackets. The pressurized CO_2 flowed from the pumps through 1/16″ OD stainless steel tubing to a check valve, a heating coil, a mixing-tee connected to the pressure relief valve, a three-way ball valve, a mixing tee (connected to the pressure transducer), and finally to the 300 mL extraction vessel described in Section 3.1.5. The pressure transducer was used to monitor the system pressure. For most of the runs the pressure relief valve was set at 17.24 MPa except for some runs at higher pressure where it was set at 25.51 MPa. The setting was chosen to ensure that the system pressure never exceeded the set maximum value. The check valve was used to protect the pumps by stopping any backflow of CO_2.



Legend

1. CO_2 cylinder
2. Filter
3. ISCO syringe pumps
4. Check valve
5. Pressure relief valve
6. Preheating coil
7. Pressure transducer
8. Three way Ball valve
9. Extraction vessel
10. Impeller
11. Thermocouple
12. Heated metering valve
13. UV-Vis detector
14. Traps (in ice water bath)
15. Mass-flowmeter/totalizer
16. CO_2 vent to fumehood
17. Heated circulating water bath
18. Thermometer
19. Data acquisition

Figure 3.4: Lab-scale supercritical fluid extraction (SFE) apparatus

The first three-way ball valve allowed the flow to be directed either to the vessel or to the bypass line. The ball valves (40 series, 17.2 MPa, 10°C to 65°C) were replaced with higher pressure and temperature resistant Swagelok ball valves (83 series, 41.4 MPa, -25°C to 120°C, Edmonton Valve and Fittings Inc., Edmonton, Alberta) to enable to work at higher temperatures and pressures. The CO_2 leaving the extraction vessel flowed to a second three-way valve that ends the separation of the main line and bypass line, and flows through an on-line UV/VIS detector where the absorbance can be measured. After flowing through UV/VIS detector, the pressurized CO_2 was passed through the heated metering valve.

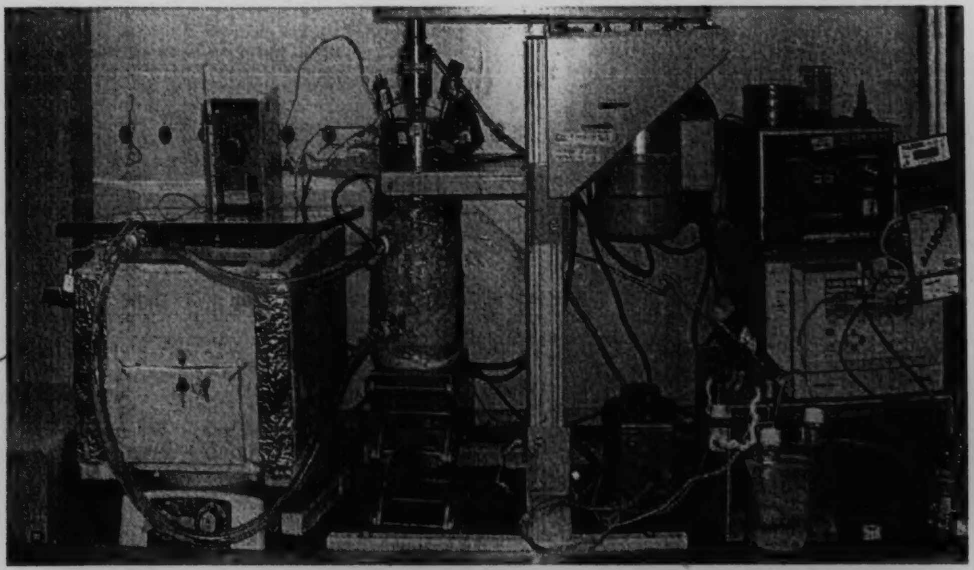


Figure 3.5: **Lab-scale Supercritical fluid extraction (SFE) apparatus**

Table 3.2: SC CO_2 extraction system components

COMPONENT	SUPPLIER	PRESSURE RATING (MPA)
CO_2 cylinder	Praxair Canada, Inc. (Edmonton, Alberta)	
Filter (0.5 micron and 10 micron)	Edmonton Valve and Fitting (Edmonton, Alberta)	
Syringe pump (ISCO 500D)	Canberra Packard (Mississauga, Ontario)	25.9
Pressure relief valve (SS-4R3A)	Edmonton Valve and Fitting (Edmonton, Alberta)	25.5
Check valves (Nupro)	Edmonton Valve and Fitting (Edmonton, Alberta)	41.4
Ball valves (Whitey)	Edmonton Valve and Fitting (Edmonton, Alberta)	17.2, 41.4
Pressure transducer (PX 502)	Omega (Laval, Quebec)	20.7
Vessel (300 mL, bolted closure)	Autoclave Engineers (Division of Snap-tite, Erie, Pennsylvania)	37.2
Thermistor probe (YSI 406)	Electrical Group, University of Alberta	
Heating circulator (HAAKE DI)	Fisher Scientific (Nepean, Ontario)	
Metering valve (Nupro)	Edmonton Valve and Fitting (Edmonton, Alberta)	41.4
Connectors etc.	Zimco Inc. (Calgary, Alberta)	
Stainless steel tubing (1/16" OD, 0.05 mm and 1 mm ID)	Fisher Scientific (Nepean, Ontario)	
155 Gilson UV-VIS detector	Mandel Scientific Company Ltd. (Guelph, Ontario)	

The CO_2 was then depressurized through the heated metering valve. The metering valve was heated to 60%-70% of the heating capacity of the rheostat so as to ensure no plugging of the metering valve due to ice formation. The depressurized CO_2 then passed through two Teflon^{TM}-taped glass trap vials immersed in an ice-cold water bath. The first trap contained glass beads (inert) and glass wool (inert) while the second trap contained 20mL toluene. Most of the extracted oil (PHCs) was collected in the first trap, while the second trap containing toluene ensured that no hydrocarbons escaping the first trap along the CO_2 flow are vented into the fumehood. The CO_2 then passed through a totalizer/mass flowmeter and was thereafter vented into a fume hood.

Water from the water bath at desired temperature was circulated through the insulated heating jacket of the vessel and the vessel was heated to the desired temperature. The temperature inside the extraction vessel was monitored using a thermistor probe inserted into the vessel. Soil samples were mixed using a MagneDrive™ mixer and an impellor (designed and manufactured by Presimax, Edmonton, Alberta) operating at 300 rpm.

All data acquisition was performed by a computer using a LabView 5.1 (National Instruments, Austin, Texas) data acquisition program. Data for the vessel pressure (from the pumps and pressure transducer), temperature (as measured by thermistor probe), flow of CO_2 (as measured by the pumps), and absorbance (from the UV-VIS detector) were collected using Lab View 5.1 software.

3.2 METHODOLOGY

The procedures used for the SC CO_2 extractions of petroleum hydrocarbons (PHCs), and for the analysis of the raw (contaminated) and SC CO_2 extracted soil samples for petroleum hydrocarbon content is described in the following sections.

3.2.1 SC CO_2 Extractions

Table 3.3 presents the conditions at which SFE experiments were conducted. Apart from experiments performed at 1 mL/min and 5 mL/min SC CO_2 flowrates, which were conducted in single cycle mode, all SFE runs were conducted in double cycle mode. Extractions carried out in single cycle mode included a 60-minute static and a 30-minute dynamic extraction, while double cycle extractions included two extraction cycles one after another. Two experiments were conducted at each extraction condition of cycle, temperature, flow and pressure. Only one SC CO_2 extraction run was conducted at 25°C and 15.2 MPa.

The extractions were performed according to the following protocol:

- Place approximately 50 g of well-homogenized contaminated flare pit soil at the bottom of the clean vessel;
- Plug vessel cover outlets 'C' and 'B' (as shown in Figures 3.2 and 3.3) with glass wool, and bolt the cover to the vessel;
- Connect CO_2 outlet 'C' to the system. The CO_2 inlet and thermistor probe are connected permanently to the vessel cover;
- Fill water bath and heat vessel to required temperature;
- Flow CO_2 into vessel at desired pressure and start the impeller at 300 rpm;
- When desired pressure and temperature conditions are reached, start the static extraction period;
- For double cycle extractions, allow a first static extraction of 60 minutes, followed by a dynamic extraction of 30 minutes. Shut all valves to allow a second static extraction of 60 minutes (in some experiments a second static

period of only 15 minutes was allowed, followed by a second dynamic extraction of 30 minutes);

- For single cycle extractions, allow a static extraction of 60 minutes, followed by a dynamic extraction of 162-270 minutes depending on the flow rate of CO_2;
- After extraction, shut all valves, stop pumps, and depressurise the vessel;
- Collect treated flare pit soil from vessel and place into a glass jar lined with Teflon tape for further analysis;
- Analyze flare pit soil samples "before" and "after" extraction, for petroleum hydrocarbon fractions F2 (C_{10}-C_{16}), F3 (C_{16}-C_{34}), and F4 (C_{34}-C_{50})
- Calculate the extraction efficiency

For SC CO_2 extractions, a 50 g soil sample is placed in the vessel. Preliminary experiments were conducted to identify the amount of soil that could be placed in the extraction vessel. The amount of soil should be such that the soil could be adequately mixed and that the extractions could be carried out successfully in a reasonable time. Experiments were conducted with different amounts of contaminated soil (20 g, 50 g, and 100 g of FP 1) and at conditions of pressure and temperature of 12.4 MPa and 13.8 MPa, and 60°C, respectively. Based on visual observations of the extracts, results suggested that extractions should be carried out using 50 g of soil. The SFE treated 100 g soil still seemed agglomerated and saturated with PHCs. On the other hand, 20 g of SFE treated soil was drier and granular as compared to 100 g treated soil. SFE treated soil weighing 50 g showed results similar to 20 g soil. Based on qualitative results, decision was made to carry out experiments with 50 g of soil.

Table 3.3: Supercritical CO_2 extraction experimental conditions

Flow (mL/min)	Pressure (MPa)	Temperature (°C)			
		25	40	60	80
FP 1					
10	11.0		✓		
	12.4		✓	✓	
	13.1		✓	✓	
	13.8		✓	✓	
	14.8			✓	
	15.2	+	✓	✓	✓
	20.7		✓		
	24.1		✓		
20	15.2		+		
5	15.2		*		
1	15.2		*		
FP 2					
10	14.8		✓		
	15.2		✓		
	24.1		✓		

✓ Double cycle extraction condition
* Single cycle extraction condition
+ Double cycle extraction condition with 15 minutes 2nd static period

In case of double cycle runs, where two extraction cycles were carried out one after another, each extraction cycle involved a 95-minute cycle, consisting of one 60-minute static extraction followed by a 30-minute dynamic extraction. Since the flare pit soil being investigated was old and weathered soil, the 60-minute static extraction time was practised to ensure that the entire 300 mL of SC CO_2 was at equilibrium with the contaminants present in the soil. The 30-minute dynamic extraction time at SC CO_2 flowrate of 10 mL/min was used to ensure that the entire 300 mL of CO_2 in equilibrium with PHCs present in the soil successfully flows out through the traps replacing the SC CO_2 in the vessel with fresh CO_2 from the pumps. The static extraction was achieved by shutting all valves downstream of the vessel while mixing continued inside the vessel (i.e. no flow of CO_2 through the vessel). The impeller at 300 rpm was started at the beginning of experiment to ensure uniform distribution of heat throughout the vessel. The CO_2 at desired pressure was then introduced into the vessel. The static period was said to begin when the pumps showed 0 mL/min CO_2 flow into the vessel and when the desired temperature of the vessel was reached. In other words, the time when the desired conditions of temperature and pressure were reached in the vessel marked the beginning of the static phase. Opening the three-way ball valve and metering valve downstream of the vessel started the dynamic extraction. The dynamic extraction was done at an average CO_2 flow rate of 10 mL/min as delivered by the pumps except for the selected runs at 20 mL/min, 5 mL/min, and 1 mL/min as described in Table 3.3.

The vessel outlet at the bottom of the vessel cover was plugged with glass wool to avoid the entrainment of fine particles. The heating rate of the variable autotransformer tape heater (Type 3PN1010, STACO Energy products Co., Dayton, Ohio) was kept at 70% of its maximum output voltage for all the extraction runs. This heating was done to ensure that the metering valve and the lines downstream of it were warm enough to prevent freezing and plugging of lines during CO_2 depressurization. This heating of the metering valve and lines helped maintain a stable flow rate through the SFE system. However, overheating of the metering valve and lines was avoided so as to minimize volatilization and/or loss of PHCs at the metering valve.

A mercury thermometer was placed in the recirculating water bath to monitor the water bath temperature and to indicate the need for any temperature adjustments (i.e. cooling with ice cubes, or turning the circulation heater off or on) in order to attain the desired temperature in the vessel.

The extracted PHCs were trapped in the first vial filled with inert glass beads lined with a layer of glass wool on top, while the second vial containing toluene ensured the trapping of any remaining PHCs in the depressurized CO_2 before it was vented to the fume hood. The glass bead traps were changed every 5-minutes. Figure 3.6 shows the picture of glass bead traps collected every 5-minutes during the 30-minute dynamic extraction period. The second trap was often refilled with toluene during the experiment to replace the toluene lost to "stripping" by depressurized CO_2.

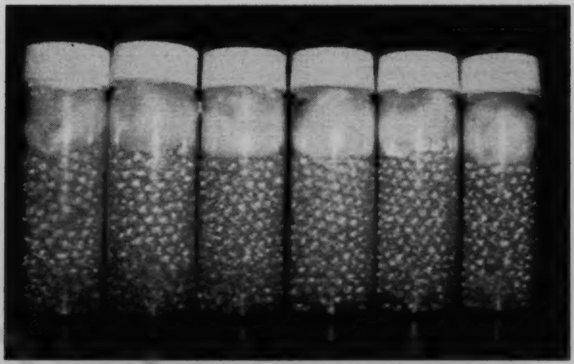


Figure 3.6: Hydrocarbons collected every 5-minutes during dynamic extraction

After the extraction, the treated soil was removed from the vessel and prepared for petroleum hydrocarbon analysis based on the *Reference Method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001c) . This preparation required that the remaining petroleum hydrocarbons present in the treated soil be extracted into toluene using soxhlet extraction (a solvent extraction process), and that the extract obtained be quantified by gas chromatography (GC/FID). Details of this procedure will be discussed further in Section 3.2.3.

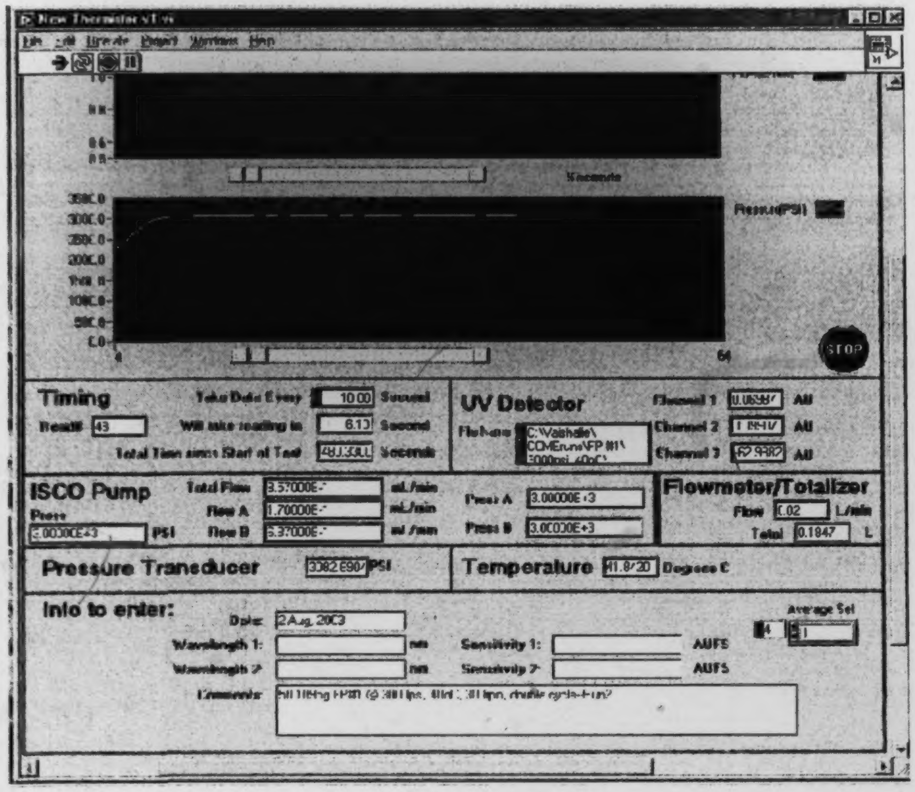
3.2.2 LabView

National Instruments LabView 5.1 software was used for data acquisition, as set-up by Savoie (2002). This software uses a graphical programming development environment based on the G programming language (Savoie 2002). It can also be used for data control, data analysis, and data presentation.

Figure 3.7 shows the LabView screen of the program used in this work. This program was developed by Roy Gitzell, a technician in the Electronics Group of the Department of Civil and Environmental Engineering, University of Alberta to be used by Savoie (2002) in her work. Data can be saved at different time intervals and can be averaged. For the experiments used in this research, data were collected every 10 seconds.

Figure 3.7 provides an illustration of the variables being used and saved during each extraction run. Comments can also be added in the comments section of the

LabView screen. LabView then saves these comments and the collected data to an Excel file where the file columns contain all the data collected. The relevant data and units are:



Reading 43

Take Data Every 10.00 Second

Flow 0.02 L/min

Total 0.1847 L

Press A 3.00000E+3

Date 2 Aug 2003

Figure 3.7: Lab View Screen

scan number (or reading number, which is a serial number to identify the particular set of parameter values measured), time (s), pump pressure (MPa), pump flow (mL/min), transducer pressure (MPa), vessel temperature (^oC), total pump flow (mL/min), pump A flow rate (mL/min), pump B flow rate (mL/min), pump A pressure (MPa) and pump B pressure (MPa).

3.2.3 Petroleum Hydrocarbon (PHC) Analysis

The petroleum hydrocarbon content of the flare pit soil prior to and following the extraction was determined by gas chromatography (GC) equipped with a Flame Ionization Detector (FID). The methodology used to analyse PHC content in the soil samples was followed according to the *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001c).

Based on this method the fractions F2, F3, and F4, representing extractable hydrocarbons from C_{10} to C_{50} present in the soil are determined by extracting a 5 g dry weight of soil sample into a 50:50 solvent mixture of acetone: hexane using the soxhlet extraction process. The solvent recovered from the soxhlet-extracted sample is passed through a column of granular anhydrous sodium sulphate to remove any water and/or polar materials if present. This recovered solvent is then concentrated to 1-2 mL in toluene using roto-evaporation process.

The solution prepared from the soxhlet extraction were then analyzed for PHC fractions (F2, F3, and F4) using GC/FID according to the method outlined in the *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001c). Based on this chromatographic analysis, the results corresponded to the concentrations obtained for three alkane windows, C_{10}-C_{16}, C_{16}-C_{34} and C_{34}-C_{50}, which were grouped as the F2, F3 and F4 fractions, respectively. The chromatograms gave results in the form of areas that were then converted to a corresponding concentration following the calculation procedure described in Section 3.2.3.2. The detailed calculation is described in Appendix A

In this work, preparation of flare pit soil samples for petroleum hydrocarbon analysis involved the following steps (all carried out at ambient conditions):

- Accurately weigh 5 g (dry weight) of raw or SC CO_2-extracted soil into cellulose extraction thimbles
- Put the thimbles into the soxhlet extraction tubes
- Place 150 mL of 50:50 acetone:hexane solvent mixture into a round bottom flask
- Let the solvent extraction process (Soxhlet extraction) run for 20 hours
- Concentrate the recovered solvent to 1-2 mL in toluene
- Quantitatively recover the concentrate and place in a volumetric flask. Dilute by a factor of 40
- Take a sample and place in a 2 mL GC auto sampler vial.
- Analyze the concentrated extract by GC/FID to determine the petroleum hydrocarbon content.

For each set of raw and SC CO_2-extracted soil samples, three sub-samples of 5 g (dry weight) each are extracted as outlined above. Three aliquots of each extract of the three sub-samples are injected into GC. This extraction of sub-samples was expected to minimize the variability in results due to the heterogeneous nature of the flare pit soils. Some of the individual steps provided above are detailed in the following Sections.

3.2.3.1 Soxhlet extraction

Soxhlet extraction ensures an intimate contact of the soil matrix with the extraction solvent due to repeated solvent vapor recovery cycles for about 20-24hrs. These cycles ensure complete transfer of PHCs from the soil to the solvent. Figure 3.8 shows a photograph of the soxhlet apparatus used in this work. Prior to using the soxhlet extraction apparatus, the apparatus was set to 4-6 cycles per hour by adjusting the heat of the individual hot plates. The plastic tubing was attached to the extractor tubes in such a way that a continuous water supply was flowed through the apparatus and maintained throughout the extraction. The water provided cooling to the body of the condenser tubes so that the vapors were continuously condensed.

Soxhlet extraction requires dry weight of the soil matrix to be analyzed. Thus, the moisture content of the soil matrix was determined before starting soxhlet extraction in order to determine the dry weight of the soil matrix used. The moisture content of the soil matrix was calculated based on the method outlined in the *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001c).

The following provides a summary of the soxhlet extraction procedure:

- Accurately weigh 5 g (dry weight) of soil into cellulose extraction thimble;
- Place the thimble into the soxhlet extractor tubes;
- Place 3-4 boiling chips into the flat bottom flask;
- Measure 150mL of 50:50 acetone:hexane solvent mixture into the 500mL flat bottom flask;

- Start the water supply (to provide cooling for condensers), and the heating system;
- Let the Soxhlet apparatus run for 20 hours;
- Cool the recovered solvent and pass it through a column of 9 g of granular anhydrous sodium sulphate.
- Rinse the sodium sulphate column with 10 mL of hexane

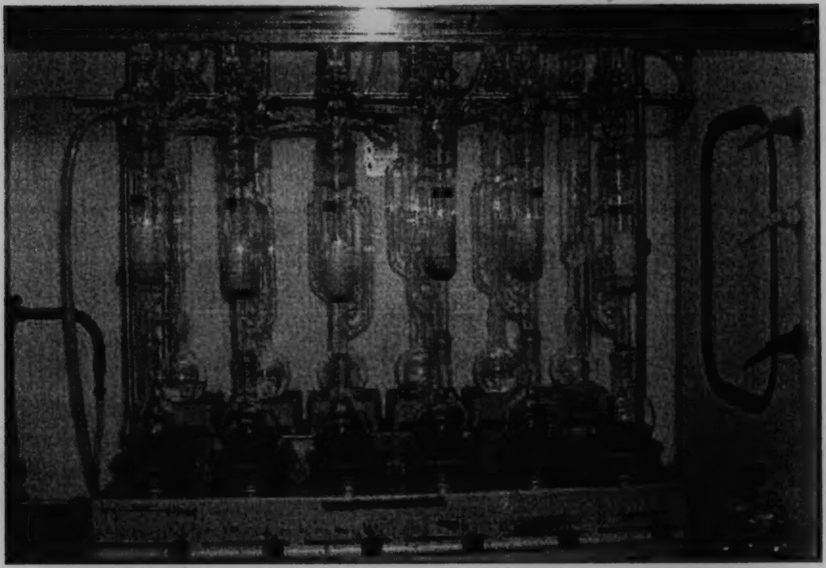


Figure 3.8: Soxhlet extraction apparatus

The recovered solvent was then concentrated to approximately 2 mL in toluene using roto-evaporator (Buchi Laboratoriums-Teenik AG, Brinkmann Instruments (Canada) Ltd., Ontario). The concentrate is then quantitatively recovered and placed in a 10 mL volumetric flask and diluted accordingly to prevent any deposition on the GC column, and then injected into GC/FID to analyse for PHC fractions.

The method of soxhlet extraction as specified by CCME (2001c) includes a step for silica gel cleanup (in-situ or column clean up) after the recovery of solvent mixture through a sodium sulphate column. This step was eliminated as it was discovered that, based on the analytical results of an inter-laboratory study on the calculation of PHC fractions in soil using *Reference method for Canada-Wide Standard for Petroleum Hydrocarbons in soil -Tier 1 Method* (CCME 2001c), it was revealed that large relative standard deviations were found in the laboratories using silica gel clean-up. Silica gel cleanup is suggested to remove aliphatic and aromatic polar compounds from the extract. It is also suggested to remove natural organic compounds (background) that are extracted by the n-hexane:acetone mixture. The silica gel clean up step can be eliminated if there is an appropriate control for background PHC concentrations. The clean flare pit soil collected from the Redwater site was used as a control sample from which the background PHC concentration can be estimated. It was therefore decided to eliminate the silica gel cleanup step in order to reduce variability in the results.

3.2.3.2 GC/FID method

GC analysis of PHCs was performed using a Varian CP-3800 gas chromatograph (Varian Inc., Mississauga, Ontario) equipped with CP-8410 model auto-injector. This is a computer controlled automated set up. The GC is equipped with a flame ionization detector (FID), which is generally used for the analysis of petroleum hydrocarbons. The Varian CP-3800 is equipped with an autosampler. The chromatographic column used in this work was a fused silica capillary low bleed chromatography column, DB 1 ht- 30 m in length, 0.32 m internal diameter, and 0.1 µm film thickness (supplied by Varian Inc. Mississauga, Ontario). This GC uses Star Chromatography Workstation Version 5 software, provided by Varian Inc., (Mississauga, Ontario). In order to work with this GC and the software, a great deal of understanding for the equipment was required. Prior to developing the final GC method, a number of test methods were performed where parameters such as column oven program, carrier gas flow rate, injection method, injection volume, and split ratio were varied.

All the procedures for equipment calibration, sample injection, data analysis and calculations for raw and SC CO_2-extracted flare pit soils, method blanks, equipment blanks and spiked samples were done according to the method provided by CCME (CCME 2001c). Samples were also sent to Enviro-test laboratories (Edmonton) for independent analysis to ensure quality control of in-house analyses.

Alkane and diesel standard preparation

Alkanes used in the analysis of PHCs were decane (nC_{10}), hexadecane (nC_{16}), tetratriacontane (nC_{34}), and pentacontane (nC_{50}). These alkanes were used as a retention time markers for retention time determinations for individual alkanes, and for calibration of the GC/FID. A mixture of n-alkanes (nC_{10}, nC_{16}, nC_{50}) was prepared as retention time standard at a concentration of 2000 ppm (mass basis). The nC_{34} retention time standard was prepared individually due to its low solubility in toluene. These standards were used for retention time determinations of individual alkanes. The standards were prepared by dissolving appropriate amounts of individual alkanes into toluene. Samples of these standards were then placed in 2 mL vials and injected into the GC. The retention time between the nC_{10} and nC_{16} peaks, the nC_{16} and nC_{34} peaks, and the nC_{34} and nC_{50} peaks constitute the retention time windows for F2, F3, and F4 PHC fractions, respectively.

Calibration standards for the GC were also prepared using mixtures of alkanes (nC_{10}, nC_{16}, and nC_{34}) at 10, 100, 500, 1000, 2000, 3000, and 5000-ppm, concentrations which correspond to the expected working range of the GC. The standards were prepared by dissolving approximately equal weights of individual alkanes in toluene (CCME 2001-c). Toluene, used as the make up solvent in a volumetric flask was also weighed using an analytical balance (Model AX 205 delta range, Mettler Toledo, Columbus, Ohio). Samples were then placed in several 2 mL GC vials that were capped for and kept for GC injections.

GC/FID Parameters

The Varian CP-3800 GC equipped with CP-8410 auto-injector has a capacity for ten 2 mL vials and three 5 mL solvent vials. Toluene being the injection solvent was placed in the solvent vials for injector syringe flushes. Of the three solvent vials only two (I and II) containing pure solvent were used as clean source for flushing the syringe. A 10μL syringe was used for injections. A total of three pre-injection and three post-injection solvent flushes were done per sample injection. Three pre-injection sample flushes of the syringe were also done. The clean solvent vials were always replaced for each set of GC sample injections.

Of the ten sample vial positions available on the autosampler, eight were used for sample vials analysis per batch, with the ninth vial position for toluene and the last one for mid-point calibration standard verification. This mid-point calibration standard verification was done to check for variations in chromatographic detections and sensitivities and hence to confirm the stability of the calibration curve. Due to the consistency of the results obtained by the calibration verification standard and hence the stability of calibration curve, the calibration verification was practiced after every 2 to 3 batches of samples. Pure toluene injections were done as blank injections between samples from each run, and to check for false-positives due to sample carry-over in the GC column.

GC/FID operation was checked and restored to normal if considerable deviations (>20% from the curve) were detected. Initially, the sample analyses were done using Method 1$^+$ but due to some instrumental error, the GC column was cut short by approximately 50cm. As a result of this, the retention times of the individual alkanes and the chromatographic detection were no longer valid, and the GC was recalibrated using Method 2*. The GC was recalibrated on 18th June 03 with method 2* (described below), where the only GC parameter that was modified was the H_2 flow rate from 20 mL/min to 30 mL/min. This increase in H_2 flow rate from 20 mL/min to 30 mL/min increased the sensitivity of the FID and hence the stability of the calibration curve.

The CP-3800 GC parameters used in this work for analysis of petroleum hydrocarbon fractions (CCME 2001c) included:

Carrier gas (Hydrogen) flow rate:	10.0 mL/min
Makeup gas (Hydrogen) flow rate:	30 mL/min
Injector temperature:	300°C

Injection solvent: toluene
Injection volume: 2.0 μL
Injection mode: Standard split/splitless
Split/Splitless Program:
  Initial: Split state ON, with split ratio of 50
  At 0.01min: Split state OFF
  At 1.00min: Split state ON, with split ratio of 50
Column temperature program:
  Initial temperature: 40°C, hold for 2 minutes
  Program: 40°C to 340°C, at 15°C/min
  Final temperature: 340°C, hold for 8 minutes
FID Detector temperature: 340°C
  Air flow rate: 300 mL/min
  H_2 flow rate: 20 mL/min^{+}, 30 mL/min*

+ Method 1: GC calibrated using above-mentioned parameters
* Method 2: GC recalibrated using above-mentioned parameters

The split/splitless injection mode was used, with an initial split ratio of 50. At injection (0.01 min), the split ratio turns off to prevent the injection solvent (toluene) and PHCs from being lost to the split bypass from the column. Although the high injector temperature of 300°C adds to the possibility of loss of solvent and lighter hydrocarbons (volatile and semi-volatile) present in the sample during injection, this high injector temperature is necessary to ensure that the heavier hydrocarbons are vaporized and carried into the column. This injection method was selected subject to meeting quality criteria for C_{50} recovery (CCME 2001c). Shutting the split instantaneously after injection ensures almost all the sample is vaporized and carried onto the column. The split state is restored one minute after injection. A 4mm injector liner with salinized glass wool

(Varian Inc., Mississauga, Ontario) as specified by CCME (2001c) was used for sample injections.

The CP-3800 GC is equipped with electronic flow control i.e. all flow rates are set and controlled electronically without the need for manual valve regulation. Ultra-high-purity hydrogen and nitrogen gases (Praxair, Edmonton, Alberta) are used, while the air used is extra dry (Praxair, Edmonton, Alberta). The ultra high purities of the gases along with the gas filters ensured negligible introduction of contaminants into the equipment.

The initial signal to noise ratio is set at 5. This ratio allows only signals with peak values 5 times greater than the detected noise to be detected as a measurable peak. Integration peak width is set at 4 seconds, which means integration of peaks is done every 4 seconds.

GC calibration

The calibration procedure for GC was performed based on *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001c). This calibration was based on the integration of area under the chromatogram between retention time markers. The mixture of nC_{10}, nC_{16} and nC_{50} alkanes standard, and individual nC_{34} alkane standard at 2000 ppm were injected according to the above-mentioned GC/FID operating parameters. This was done to establish the retention time for these alkanes, thereby defining the C_{10}-C_{16}, C_{16}-C_{34} and C_{34}-C_{50} retention time windows for fractions F2, F3 and F4, respectively.

Calibration standards using mixture of equal weights of alkanes (C_{10}, C_{16}, C_{34}) in toluene were prepared at seven concentrations (10, 100, 500, 1000, 2000, 3000, 5000 ppm). These calibration standards were also injected by the above-mentioned method and data were stored for analysis by the Star Chromatography software. This calibration is based on integration of area under the chromatograms between the retention time windows (CCME 2001c) established between C_{10}-C_{16}, C_{16}-C_{34}, and C_{34}-C_{50}, respectively. According to USEPA (1996b), the integrated areas for each retention time window includes the unresolved complex mixture ("hump") that lies below the individual peaks. This "hump" is due to the presence of several chromatographically unresolved components that might be present along with other compounds that will produce well-resolved peaks in GC/FID chromatogram (USEPA 1996).

The area of all peaks eluting between the retention time markers i.e. nC_{10} to nC_{16}, nC_{16} to nC_{34}, and nC_{34} to nC_{50} were summed up. A horizontal baseline was projected between each retention time window so as to integrate all the peak areas. In other words, F2 (C_{10}-C_{16}) hydrocarbons were determined by integration of all area counts from apex of the nC_{10} peak to the apex of nC_{16} peak. F3 and F4 were determined similarly using areas from nC_{16} to nC_{34} and from nC_{34} to nC_{50}.

According to CCME (2001c), "*mandatory instrument performance criteria for nC_{10} to nC_{50} are that nC_{50} response factor must not be less than 70% of the average of nC_{10}, nC_{16}, and nC_{34} response factors and the nC_{10}, nC_{16}, and nC_{34} response factors must be within 10% of the average response for the three compounds. This performance criteria must be met by any injection system used for hydrocarbon analysis and* *confirmed on a daily basis*". For F4 fraction (C_{34}-C_{50}) results, the chromatogram should descend to baseline by the retention time of C_{50} (CCME 2001c).

For each hydrocarbon standard alkanes (nC_{10}, nC_{16}, and nC_{34}), within each of 7-point calibration curve runs, response factor (RF) is calculated and an average of all these response factors (RFs) is taken. Thus, there are 21 individual RFs to be averaged. Each individual RF is calculated as:

$$\mathrm{RF} = \frac{A}{C} \qquad (1)$$

Where, A = the area under individual n-alkane peak

C = the concentration of the individual n-alkane standard (g/mL)

The average response factor is calculated as:

$$\mathrm{RF_{avg}} = \frac{\text{sum of individual RF values}}{\text{number of RF values used}} \qquad (2)$$

This average RF is used to calculate the total hydrocarbons present in each of the carbon ranges C_{10} to C_{16}, C_{16} to C_{34} and C_{34} to C_{50}. The calculation for PHCs present in a sample is shown below:

$$\textbf{For F2, } \mathbf{C_{10}\text{-}C_{16}} \textbf{ hydrocarbons (mg/kg)} = \frac{A_{C10-C16} \times Vol \times F}{RF_{avg} \times W_d} \qquad (3)$$

$$\textbf{For F3, } \mathbf{C_{16}\text{-}C_{34}} \textbf{ hydrocarbons (mg/kg)} = \frac{A_{C16-C34} \times Vol \times F}{RF_{avg} \times W_d} \qquad (4)$$

For F4, C_{34}-C_{50} hydrocarbons (mg/kg) = $\dfrac{A_{C34-C50} \times Vol \times F}{RF_{avg} \times W_d}$ (5)

Where,

$A_{C10\text{-}C16}$ = the integration of all area counts from the apex of the nC_{10} peak to the apex of the nC_{16} peak

$A_{C16\text{-}C34}$ = the integration of all area counts from the apex of the nC_{16} peak to the apex of the nC_{34} peak

$A_{C34\text{-}C50}$ = the integration of all area counts from the apex of the nC_{34} peak to the apex of the nC_{50} peak

Vol = Final volume of sample extract (mL)

F = Dilution factor applied to bring the samples and standards into appropriate peak height range

RF_{avg} = Average response factor calculated above

Wd = Dry weight of sample taken (g)

The detector response i.e. the average area counts for each n-alkane was plotted against their corresponding concentrations to generate the linear calibration using a least squares regression method (CCME 2001c). Three injections of each calibration standard were performed and the corresponding area counts obtained were averaged and calculated for individual RFs (equation 1). Linearity for single compounds was checked to be within 10%.

Thus areas for individual F2, F3, and F4 fractions were obtained by integrating the chromatograms and the corresponding concentration for each fraction was calculated using the above calculation procedure. A sample of detailed calculation is provided in Appendix A. After calibration of GC, the linearity of the detector response was also checked using motor oil calibration standards (1000, 2000, 3000, 5000 ppm). These standards were prepared by weighing appropriate amounts of motor oil into toluene. The samples were injected and analyzed for PHC fractions using the above-mentioned procedure. Linearity was checked to be within 15% for each of the calibrated carbon ranges (F2, F3, F4) for motor oil (CCME 2001c). The GC calibration and the method validation criteria will be discussed in detail in Sections 4.2.2 and 4.2.3.

Sample and blank injections

Toluene extracts of the raw and SC CO_2 extracted flare pit soil samples were placed in 2 mL autosampler vials and were injected in triplicates using the chromatographic conditions defined for standards calibration. The detector response area calculations for the soil sample and blank injections were done in exactly the same way as for the alkanes and motor oil calibration standards, by integrating the area counts between each of the retention time windows. Thus, based on the extraction procedure and the above-mentioned protocol outlined in Section 3.2.3, the concentration of petroleum hydrocarbons fractions (F2, F3, and F4) in the toluene extract of the samples is determined. Detailed calculations are presented in Appendix A.

Quality control

The quality control criteria described below must be demonstrated before and during analysis (CCME 2001c). The method detection limit (MDL) for the analysis must be experimentally determined before analyzing samples. Laboratories must achieve either an MDL that is 20% of the applicable soil type as described in the CWS for PHC (CCME 2001a), or an MDL as given in CCME (2001a), 'whichever is higher'. Based on CWS-PHC, for coarse-grained surface soil in an industrial area, the required F2, F3, and F4 values are 760, 1700, and 3300 mg/kg and the corresponding MDLs are 152, 340 and 660 mg/kg (20% of the applicable soil type). The MDLs according to CCME (2001c) must be met as follows:

➢ F2, C_{10} to C_{16} hydrocarbons	3.9 mg/kg
➢ F3, C_{16} to C_{34} hydrocarbons	9.0 mg/kg
➢ F4, C_{34} to C_{50} hydrocarbons	8.0 mg/kg

Modification to these quality control criteria were applied in this work based on personal communications with Ted Nason (Alberta Environment) and Richard Turle (CCME, Analytical Methods and Advisory Group, Ottawa, Ontario). Due to the difficulty encountered in spiking the required concentrations for MDLs for each of the PHC fractions, the MDLs for each fraction using GC/FID were not detected. However, to confirm the accuracy of measured hydrocarbon contents, clean sand spiked with known amounts of weathered diesel oil, were solvent extracted and GC-injected in triplicates, The results obtained in-house and from the commercial lab for the spiked soil were similar, which confirms the validation of the GC method being used, and confirms the accuracy of the results obtained in-house.

Method blanks were also injected in the GC to investigate if positive errors were added by the method. These method blanks were samples that did not contain any soil but had followed the same methodology of soxhlet extraction, roto-evaporation, and finally GC analysis.

Performance samples are sample blanks, which are clean sand samples presumably without any hydrocarbon content. These sample blanks were solvent-extracted and analyzed to ascertain that sand used for spiking have no substantial hydrocarbon content.

A calibration verification standard (i.e. a midpoint alkane calibration standard used for initial calibration) with a known concentration is injected per batch of ten sample vials. If this calibration verification standard deviated by more than 20%, the calibration curve was rerun or restored to the appropriate conditions if possible.

Commercial analysis of the PHC fractions present in the samples were also done according to CCME method (CCME 2001c). Samples were sent to Eviro-Test Laboratories Inc., (Edmonton, AB) for petroleum hydrocarbon fractions (F2, F3, and F4) analysis. This commercial analysis was to confirm the efficacy and accuracy of the laboratory protocols and analysis method developed and practiced in-house.

CHAPTER 4. RESULTS AND DISCUSSION

The following chapter presents the results of the experiments conducted in this study and provides a discussion of these results.

4.1 SC CO_2 EXTRACTION OF PHCS FROM FLARE PIT SOILS

Various studies have obtained optimal conditions for SC CO_2 extraction of PHCs from contaminated soil. Literature suggests that the pressures ranging from 15.2 MPa to 40.5 MPa and temperatures ranging from 40°C to 150°C are considered optimal for SFE of petroleum hydrocarbons (n-alkanes ranging from C_6 to greater than C_{34}) from contaminated soils (Morselli et al. 1999; Low and Duffy 1995; Eckert-Tilotta et al. 1993; Lopez Avila et al. 1993). Most of the work on SC CO_2 extraction of PHCs has been conducted on spiked soils. Very few SFE experiments reported in the literature to date have dealt with SC CO_2 extraction from real soils directly obtained from the contaminated site. No work on remediation of flare pit soil using SC CO_2 has been published yet.

This work is considered to be the first published work on remediation of flare pit soil using SFE. Thus, supercritical carbon dioxide extractions of petroleum hydrocarbon (PHC) fractions, F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}) and F4 (nC_{34}-nC_{50}) from flare pit soils were conducted at temperatures of 40°C, 60°C and 80°C, and pressures ranging from 11.0 MPa to 24.1 MPa. This range of extraction conditions helped in determining the optimal extraction conditions for extraction of PHC fractions F2, F3, and F4 from flare pit soils. Pressures above 24.1 MPa and temperatures above 80°C however could not be investigated because of the limitations of the syringe pumps and recirculating water bath, used for this work.

The following sections describe the results obtained for the supercritical carbon dioxide experiments conducted in this work. An example of Excel data file, one of the files collected during an extraction experiment is provided in Appendix B.

4.1.1 Pressure Data

Two sets of pressure data, one from the ISCO syringe pumps and the other from the pressure transducer, were collected and recorded using the LabView data acquisition software. The pressure data from the syringe pumps (A and B) indicates the pressure at which the CO_2 is being delivered to the vessel, while the data from pressure transducer indicates the pressure immediately upstream of the extraction vessel. Figures 4.1 and 4.2 show the sample pressure data for a single cycle extraction (at 15.2 MPa and 40°C) and a double cycle extraction (at 20.7 MPa and 40°C), respectively. Most of the extraction experiments conducted in this work were double cycle extraction experiments except for the set of experiments conducted at 15.2 MPa and 40°C where the CO_2 flow rates were 5 mL/min and 1 mL/min.

The pumps A and B are designed such that they can be set at "Constant Flowrate mode" or "Constant Pressure mode". In this work, the pumps were set at "Constant Pressure mode", so that SC CO_2 was delivered at a constant pressure throughout the

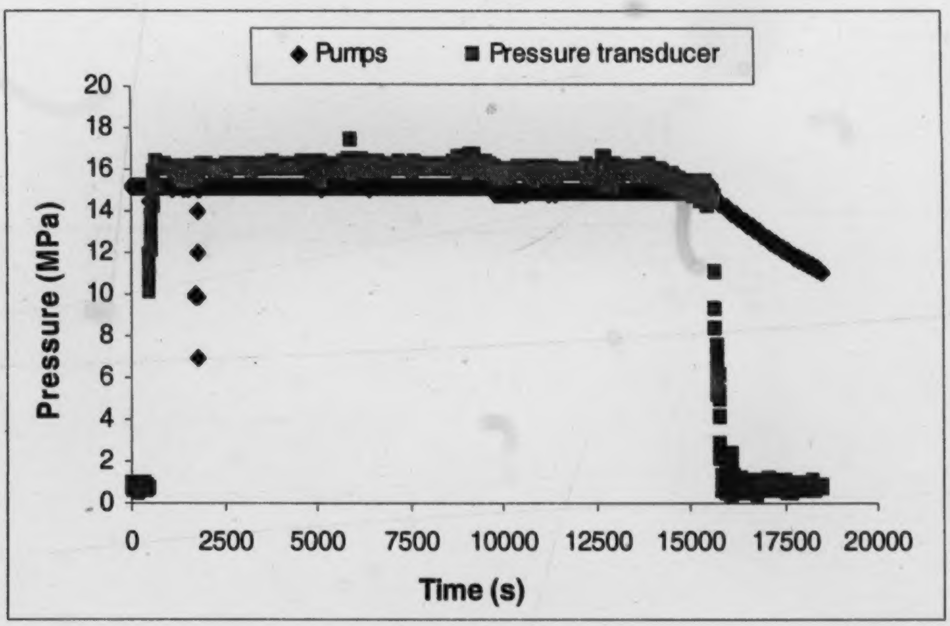


Figure 4.1: **Sample pressure data for a single-cycle SC CO_2 extraction (at 15.2 MPa and 40°C , 2003-06-27)**

experiment, independent of which pump is running. Both pumps A and B run independent of each other, but simultaneously to ensure constant supply of CO_2.

The data obtained from the pressure transducer exhibit offsets in pressures in comparison to the pressures indicated by pumps A and B. The pressure transducer reading was observed to show an offset of +0.6 MPa to +0.9 MPa when pump B was running, and +0.4 MPa to +0.6 MPa when pump A was running. During the extraction runs, the LabView program was started after both the pumps had been refilled and pressurized to desired pressure. During the refilling of the pumps, the pressure in the pumps drops to that of CO_2 cylinder, to approximately 6.1 MPa.

In Figure 4.1, the pump pressure is already set at the desired extraction pressure of 15.2 MPa. Usually, while pressurizing the pumps to the desired pressure, the pump pressure quickly rises and stabilizes in about 60 s. The pressure transducer indicates a pressure of 0.8 MPa existing in the lines at the beginning of the extraction run. With pump B running first, the CO_2 flow is then opened to the vessel at 651 s. As shown in Figure 4.1, the pressure in the vessel (as indicated by the pressure transducer) gradually rises to about 16.1 MPa, and stabilizes. This reading is 0.9 MPa higher than the pump pressure of 15.2 MPa, but this offset is however in agreement with the repeated observations of transducer readings indicated in all extraction runs.

During the static extraction period, at 1700 s, all the valves were shut and pump B was refilled. As mentioned above, the pump pressure drops to the pressure in the CO_2 cylinder (6.1 MPa) while refilling (see Figure 4.1). After refilling and repressurizing the pump, the CO_2 flow is opened to the vessel. The pressure transducer reading remains stable at 16.1 MPa until pump B runs out of CO_2 at 9800 s and stops running. Since pump A and B are running in independent mode at constant pressure, pump A compensates for empty pump B and keeps pressure stable at 15.8 MPa. This reading as measured by pressure transducer is +0.6 MPa higher than the pump pressure (15.2 MPa), and thus indicates a drop from transducer reading of 16.1 MPa (pump B) to 15.8 MPa (pump A). This offset for pump A was not confirmed by repeated observations in other extraction experiments in this work because all the other extraction experiments conducted were double cycle experiments, where only pump B was used in order to avoid any offsets arising from changing pumps.

The pressure in the vessel remains stable until the end of the extraction at about 15,000 s, when the pumps are stopped and the vessel is depressurized. Figure 4.1 shows a drop in the pressure transducer reading as the vessel is being depressurized and returns to the residual pressure of 0.8 MPa that was originally found in the system.

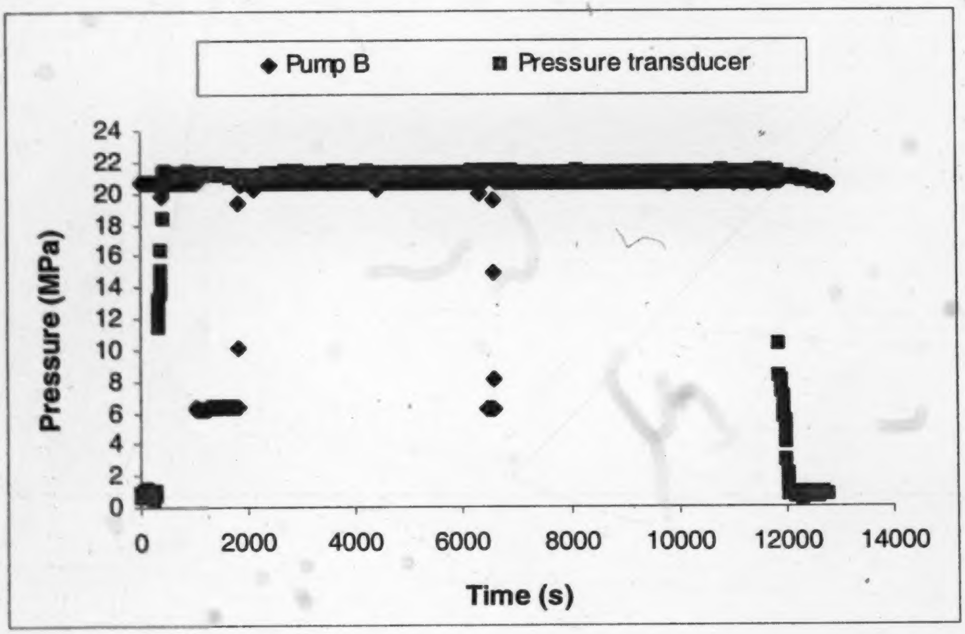


Figure 4.2: **Sample pressure data for a double-cycle SC CO_2 extraction (at 20.7 MPa and 40°C, 2003-06-27)**

The same observations were made for double cycle extraction runs. As mentioned earlier, most of the extraction experiments were double cycle extractions, to avoid any offsets arising from changing pumps, only pump B was used during the extractions. Figure 4.2 for a double cycle extraction is similar to Figure 4.1 for a single cycle extraction except that in double cycle extractions only pump B is being used instead of both pumps A and B. In double cycle extractions, during the first static extraction period, all valves are shut and pump B is refilled at around 980 s. This refilling caused the pump pressure to drop to the cylinder pressure of about 6.1 MPa. The pumps were then repressurized to 20.7 MPa. The pressure transducer reading is observed to be at 0.8 MPa at the beginning of the extraction, and increases to 21.4 MPa when the pump is open (at 530 s) to the vessel. This reading is 0.7 MPa higher than pump B pressure, thereby showing an offset of the pressure transducer as mentioned previously. During the second static extraction period, all the valves are shut again and pump B is refilled and repressurized at about 6300s. The pump pressure and the transducer pressure remained stable throughout the extraction, except for when refilling and re-pressurizing the pumps. At the end of the extraction, the pumps are stopped and the vessel is depressurized as a result of which, the pressure transducer reading drops to its original reading of 0.8MPa as observed at the beginning of the extraction. The pressure transducer offset for pump B was observed during all extraction conditions of temperature and pressure, suggesting that it is independent of the extraction conditions.

4.1.2 Flow Data

Flow data is received from ISCO syringe pumps, which measures the CO_2 flowrate from the pumps at the desired extraction pressure and at 7.5°C. The data are recorded using the LabView data acquisition software. Figures 4.3 and 4.4 show the sample flow data for a single cycle extraction on a full scale and on a reduced scale. Figures 4.5 and 4.6 show the sample flow rate data for a double cycle extraction on full scale and on a reduced scale.

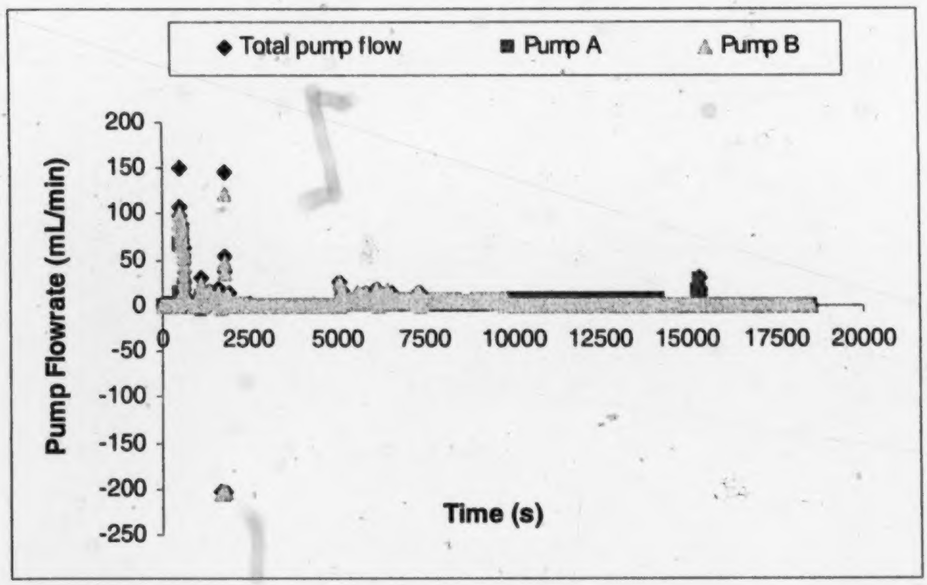


Figure 4.3: **Pump flow data for single-cycle (2003-06-27) extraction (full scale)**

The maximum flowrate at which the pumps are set to allow refilling of CO_2 from CO_2 cylinder is –204 mL/min. This value is also the maximum value at which the CO_2 can be delivered into the vessel. The combined flow of both the pumps (A and B) is the total pump flow. Figure 4.3 shows that the CO_2 is being introduced into the pumps at about 480 s at total pump flow of +150 mL/min. During the static extraction period, pump B is stopped, refilled, and repressurized. The total pump flow (pump B) of –200 mL/min indicates the refilling of the pump at 1700 s.

The desired total flowrate from the pumps during dynamic extraction is 5 mL/min for the single cycle extraction illustrated in Figure 4.4 and 10 mL/min for the double cycle extraction illustrated in Figure 4.6. The flow patterns (on a reduced scale) for the single cycle experiment (Figure 4.4) show that the desired CO_2 flowrate ranges from 4.5

mL/min to 6 mL/min from 5000 s to 15000 s. This duration reflects the dynamic extraction period. The initial instability of the flowrate during dynamic extraction was due to the manual fine-tuning of the metering valve to obtain the desired total CO_2 flowrate. As mentioned in Section 4.1.1, as pump B runs out of CO_2 at 9800 s, pump A starts running and maintains the steady flow of CO_2 into the vessel at the desired pressure.

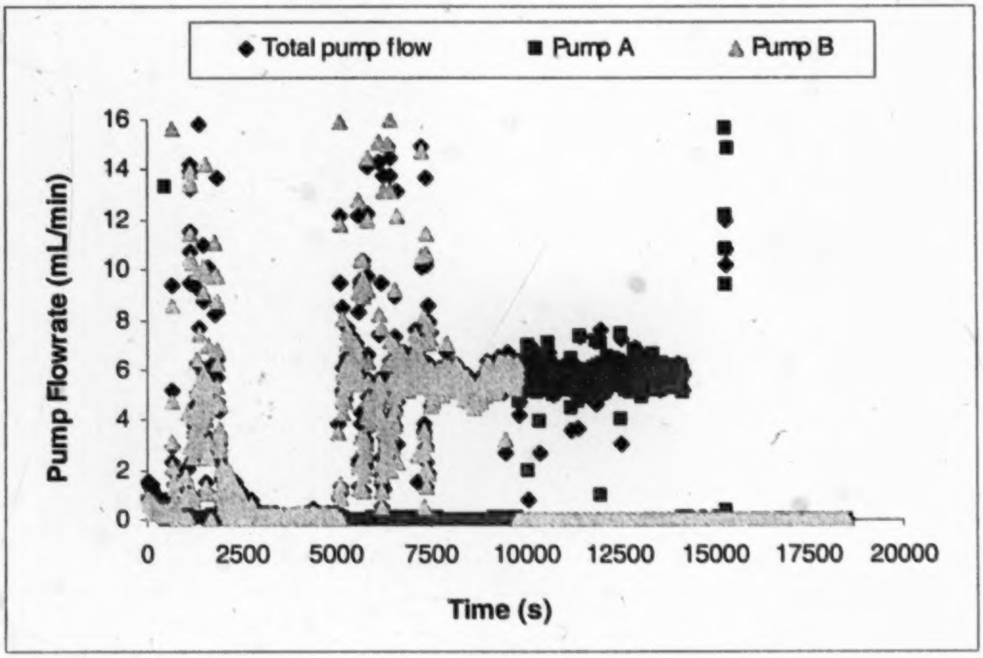


Figure 4.4: **Pump flow data for single-cycle (2003-06-27) extraction (reduced scale)**

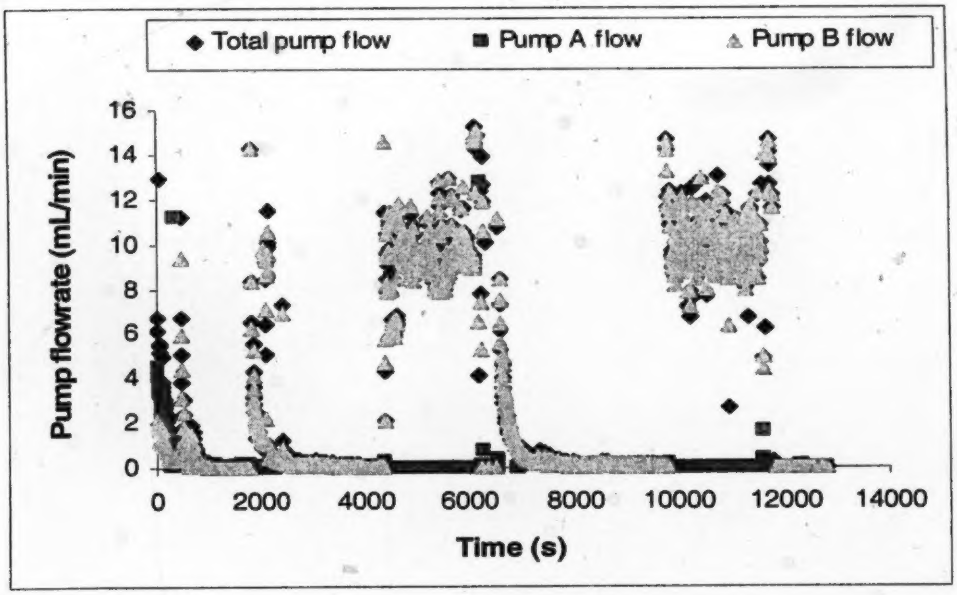


Figure 4.5: **Pump flow data for double cycle (2003-08-02) extraction (full scale)**

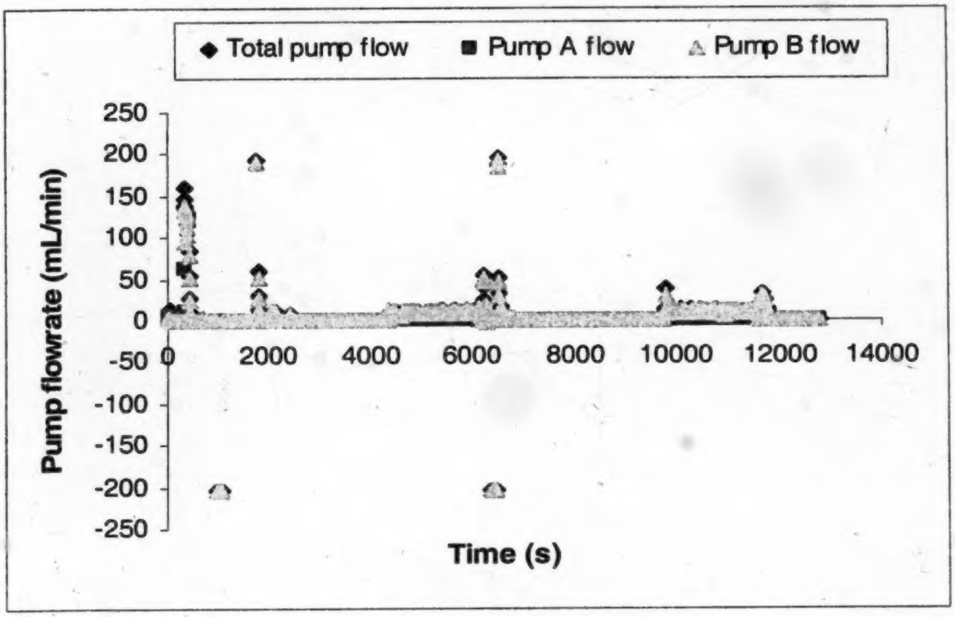


Figure 4.6: **Pump flow data for double cycle (2003-08-02) extraction (reduced scale)**

For the double cycle experiments on reduced scale, Figure 4.6 shows a similar flow pattern but the desired flowrate of 10 mL/min ranges from 8 mL/min to 11 mL/min during the dynamic extraction. The two ranges of flowrate between 4000 s to 6000 s and 10000 s to 12000 s indicate the two dynamic extraction periods. In the case of the double cycle extraction, pump B is refilled twice. During each static extraction period (1000 s to 4000 s, and 6000 s to 10000 s), pump B is refilled (-200 mL/min) and repressurized (+200 mL/min) at 1000 s and 6300 s (see Figure 4.2). At the end of each dynamic extraction, Figures 4.4 and 4.6 show an increase in flowrate. This increase in CO_2 flowrate indicates the bypass flow, which is usually carried out at higher flowrate than the experimental flowrate in order to clean the lines downstream of the vessel if plugged with any PHCs.

4.1.3 Temperature data

The extraction temperature inside the vessel was continuously monitored using a thermistor probe permanently inserted into the vessel. The temperature data were collected and recorded using the LabView data acquisition software. Temperature data collected during single cycle and double cycle extractions are shown in Figure 4.7 and Figure 4.8. The vessel was heated to the desired temperature by a circulating hot water through the recirculating jacket surrounding the vessel. The heated water came from a hot water bath maintained at the desired temperature.

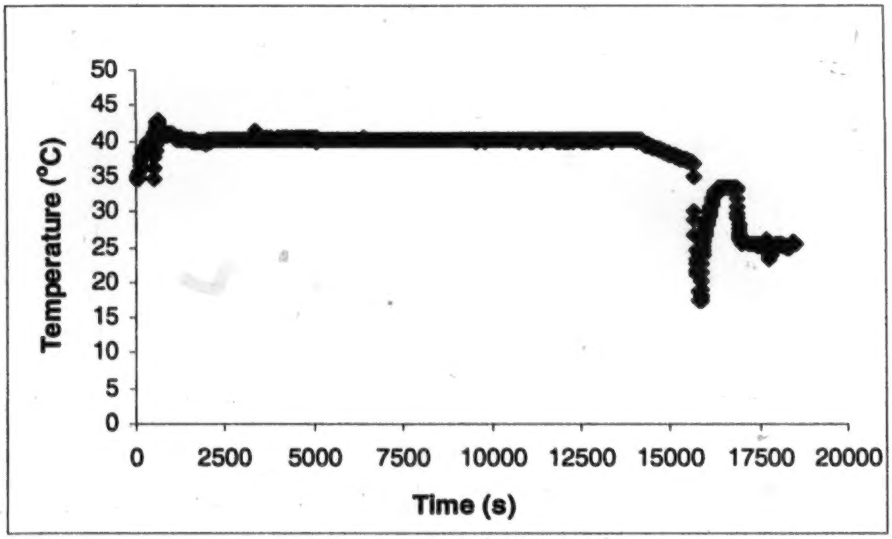


Figure 4.7: Temperature data for single cycle extraction (2003-06-27)

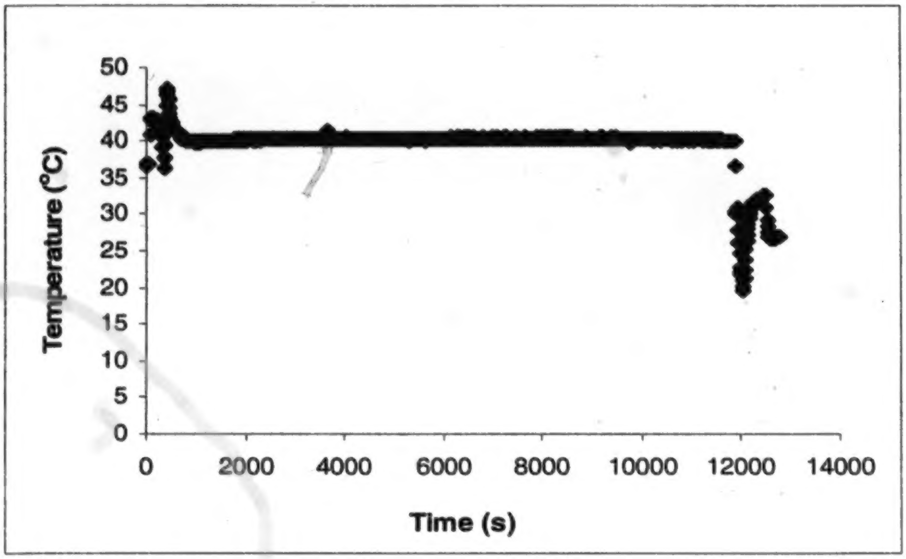


Figure 4.8: Temperature data for double cycle extraction (2003-08-02)

The use of a hot water recirculating jacket allowed running extractions at temperatures ranging from 25°C to 80°C. The water bath was controlled and also visually monitored using a mercury thermometer that was placed directly in the water bath. Any adjustments in water temperature were done by adding ice cubes or by increasing the temperature of the heat controller as required.

In both Figures 4.7 and 4.8, a rise in temperature in the vessel from 36°C to 43°C during the single cycle extraction and from 36°C to 47°C during the double cycle extraction was observed. This rise in temperature is observed at all extraction conditions when the high pressure CO_2 is introduced into the vessel at the beginning of the extraction. The temperature increases gradually and then decreases back to the set temperature in the water bath (at 40°C in Figures 4.7 and 4.8) as the extra heat is lost to the surrounding environment. A similar temperature pattern was observed by Savoie (2002) and Odusanya (2003) in their work. This increase in temperature is due to the sudden rise in pressure in the vessel when the pumps are open into the vessel. With the pressure of the double cycle extraction, being higher (20.7 MPa, Figure 4.1) than for the single cycle extraction (15.2 MPa, Figure 4.2), the temperature increase seen in double cycle extraction experiment is larger than for single cycle experiment. It is believed that this rise in temperature is due to the sudden pressurization by the CO_2.

4.1.4 Visual Observations

4.1.4.1 Observations of the flare pit soils before and after SC CO_2 extraction

Visual observations of the two flare pit soils under investigation were made prior to and following extraction. Figures 4.9 and provide a visual representation of FP 1 and FP 2 prior to and following SC CO_2 extraction. In Figure 4.9, the FP 1 (shown on the left) is the contaminated flare pit soil prior to extraction by SC CO_2. It appeared as dark, grainy sand where the sand particles were agglomerated together due to the PHCs present in the soil. Contaminated FP 2 shown in Figure 4.10 (on the left) was a darker (dark brown-black) coloured loam. Both the soils had a strong characteristic petroleum hydrocarbon odour. Following the completion of SC CO_2 extraction, treated FP 1 (Figure 4.9, on the right), appeared drier, grainier and much lighter in color, whereas FP 2 appeared as a fine, coffee-like powder (Figure 4.10, on the right), also drier, and lighter in color.

4.1.4.2 Observations of the extracted PHCs

The PHCs extracted from the flare pit soils during SC CO_2 extraction were trapped in glass vials filled with glass beads. The top of these glass beads was layered with glass wool to prevent any escape of PHCs along with the flow of CO_2. Figure 4.11 shows the glass bead traps containing PHCs collected every five minutes during 30 minutes of dynamic extraction.

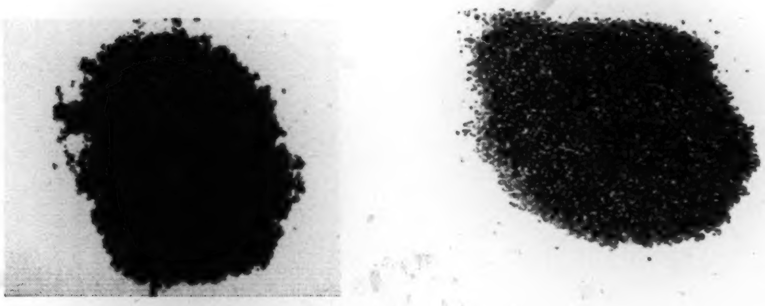


Figure 4.9: Flare pit soil 1 before and after extraction

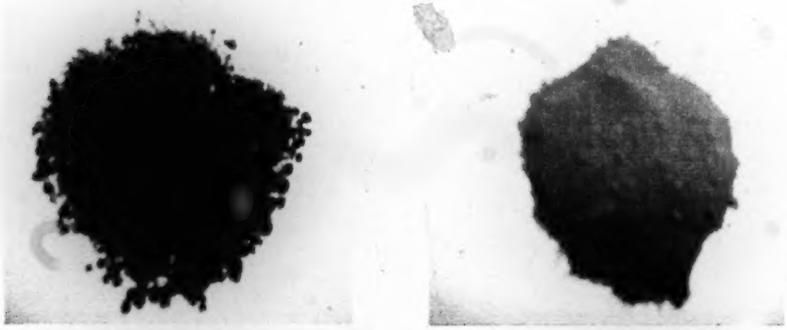


Figure 4.10: Flare pit soil 2 before and after extraction

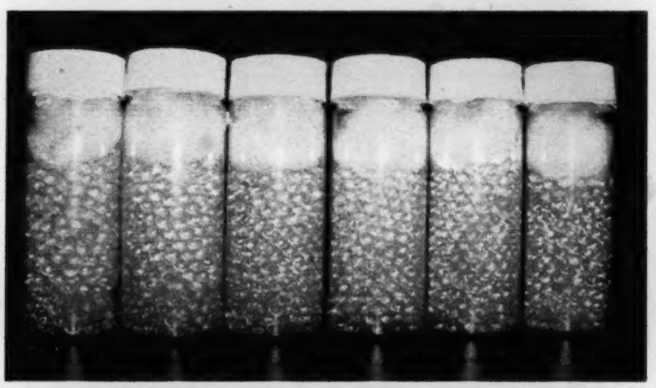


Figure 4.11: PHCs collected during SC CO_2 extraction

Visual observations of the PHCs collected in the vials showed a difference in colour of the PHCs collected during dynamic extractions. Extractions at lower pressure yielded lighter coloured oil (light yellow), which darkened with an increase in extraction pressure (dark yellow/brown). Similar effects in colour difference were observed by Elkanzi and Singh (2001) and Hwang et al. (1995). They suggested that these color differences might provide visual evidence of compositional variations as a function of time.

4.2 PETROLEUM HYDROCARBON ANALYSES

Flare pit soil samples were analyzed for petroleum hydrocarbon fractions F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}) and F4 (nC_{34}-nC_{50}), before and after SC CO_2 extraction using soxhlet extraction followed by gas chromatography/flame ionization detection (GC/FID). The PHC contents before and after SC CO_2 extraction were then used to calculate the extraction efficiency.

Glass traps containing PHCs collected during different extraction conditions at different time intervals during the dynamic extractions were also analyzed by gas chromatography. The analysis was performed to determine if different fractions of PHCs were extracted at different times throughout the dynamic extraction.

The following sections will discuss the results of the PHC analyses. First, the important parameters necessary for PHC content calculation will be presented followed by a discussion of the effects of the factors such as pressure, temperature, supercritical fluid density, CO_2 flow rate, and soil type on the extraction efficiency of PHCs.

4.2.1 Alkane Retention Time

Figure 4.12 shows the chromatograms of the retention time standards The first retention time standard was a mixture of appropriate amounts of decane (nC_{10}), hexadecane (nC_{16}) and pentacontane (nC_{50}) standards. The mixture contained 2000 ppm of decane and hexadecane n-alkane concentrations, and 15 ppm and 17.5 ppm of pentacontane in Method 1 and Method 2, respectively. The second retention time standard for tetratriacontane (nC_{34}) was made separately due to the unknown solubility of nC_{34} in toluene. The smallest peak of nC_{50} (Figure 4.12) reflects the very low concentration of 15 ppm and 17.75 ppm in Method 1 and Method 2, respectively. The retention time chromatograms for n alkanes shown in Figure 4.12 reflect the retention times obtained for n-alkanes (nC_{10}, nC_{16}, nC_{34}, nC_{50}) using the Methods 1 and 2. The GC parameters used in Method 1 and Method 2 have already been provided in Section 3.2.3.2. As mentioned in Section 3.2.3.2, Method 2 was followed for sample analyses after GC column was cut short and recalibrated using method 2. As a result of the reduction in the column length, a shift in the retention times of n-alkanes was observed. This shift can be clearly seen in the chromatograms obtained for the respective n-alkanes using Method 1 and 2 (Figure 4.12)

The retention times of the n-alkanes were determined from the chromatograms shown in Figure 4.12. The retention times are provided in Table 4.1 and are averages of 4-5 retention time runs.

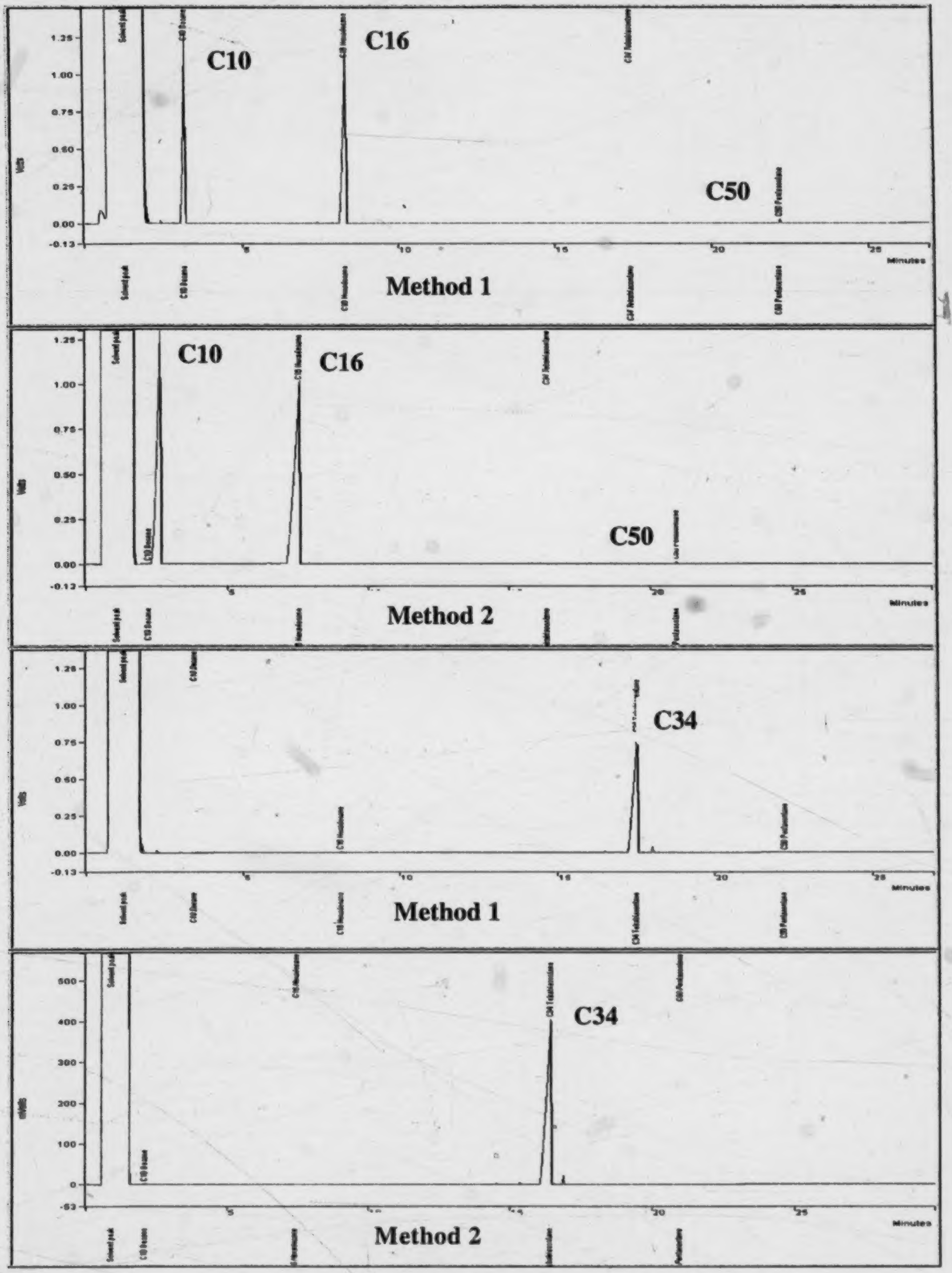


Figure 4.12: nC_{10}, nC_{16}, nC_{34}, and nC_{50} retention time chromatograms obtained using method 1 and method 2

Table 4.1: Retention times of n-alkanes

n-ALKANE PEAK	RETENTION TIME (min.)
METHOD 1	
Toluene (injection solvent)	1.1
nC_{10}	2.7
nC_{16}	7.9
nC_{34}	17.4
nC_{50}	21.8
METHOD 2	
Toluene (injection solvent)	0.94
nC_{10}	2.4
nC_{16}	7.2
nC_{34}	16.4
nC_{50}	20.9

4.2.2 GC/FID Calibration

The GC calibration method described in Section 3.2.3.2, was performed according to the *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method* (CCME 2001-c). This calibration is based on the integration of the area under the chromatogram between retention time markers (nC_{10}-nC_{16}, nC_{16}-nC_{34} and nC_{16}-nC_{50}). Calibration standards were the mixtures of n-alkanes (nC_{10}, nC_{16}, nC_{50} and nC_{34}) ranging from 10 ppm to 5000 ppm and were injected using Method 1 and Method 2 (after recalibrating GC). The n-alkane, nC_{50} was used solely as a retention time marker and a response factor standard for nC_{10}-nC_{50} HCs. The area counts obtained for the individual alkanes were plotted against their respective concentrations to obtain linear calibration curves. Figures 4.13 and 4.14 show the calibration curves obtained for the individual n-alkanes at the respective concentrations, using Method 1 and Method 2, respectively.

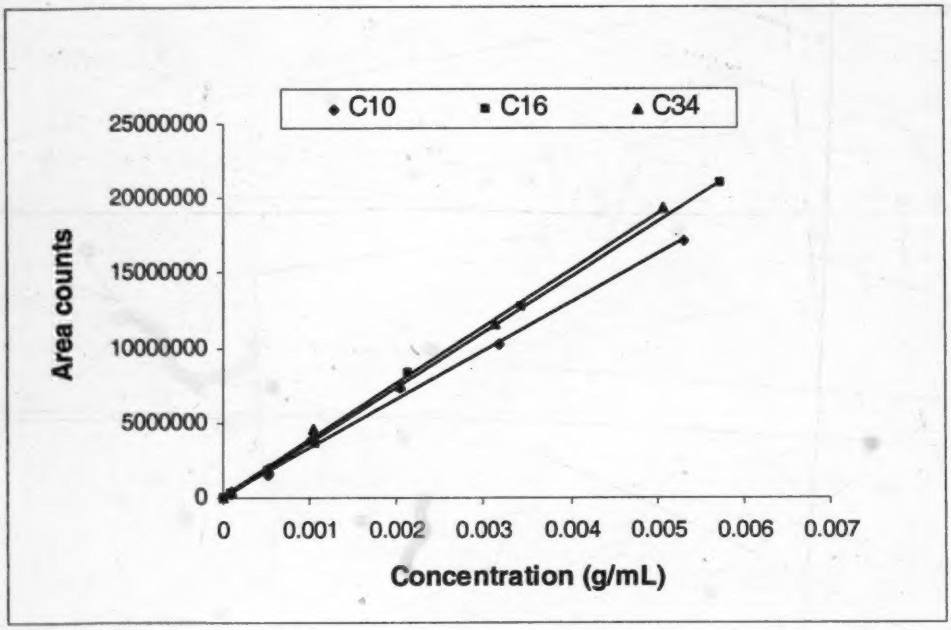


Figure 4.13: **GC/FID n-alkane (nC_{10}, nC_{16}, nC_{34}) standards calibration curves (Method 1)**

For GC calibration according to CCME (2001c), the following criteria should be met:

Criteria 1 (Linearity)

- Linearity should be within 10% for single compounds. The single compounds used in this research are nC_{10}, nC_{16} and nC_{34}.

- Linearity should be within 15% for each calibrated carbon ranges (F2, F3, F4) for the products (in this case, motor oil).

Criteria 2 (Mandatory instrument performance criteria for nC_{10}-nC_{50} HCs)

- RF values obtained for individual n-alkanes (nC_{10}, nC_{16}, nC_{34}) should be within 10% of each other.
- C_{50} RF should be no less than 70% of the average of nC_{10}, nC_{16}, and nC_{34} (RFavg).

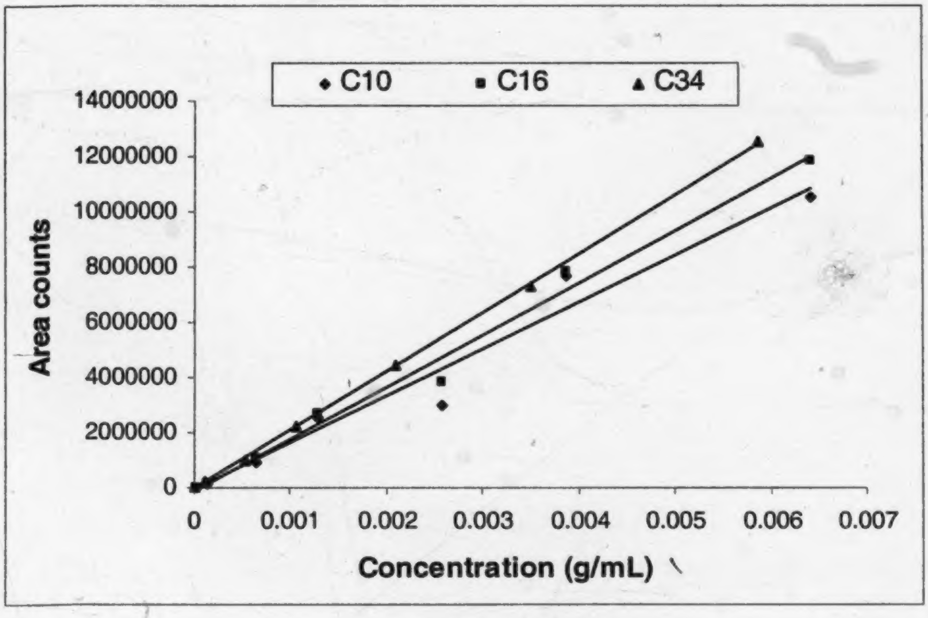


Figure 4.14: GC/FID n-alkane (nC_{10}, nC_{16}, nC_{34}) standards calibration curves (Method 2)

Table 4.2 and Table 4.3 show the linear correlation coefficients for the single compounds (nC_{10}, nC_{16}, nC_{34}) and products (motor oil) as required by the first criteria. In this work, the linearity was based on the linear regression (R^2) coefficients obtained for F2, F3, and F4 fractions of PHCs. If the R^2 values obtained were found to be greater than 0.9 for single compounds (n-alkanes) and greater than 0.85 for F2, F3, and F4 fractions of PHCs in motor oil, Criteria 1 was said to be met. Both Tables 4.2 and 4.3 show that Methods 1 and 2 used for analyzing PHC contents met the required CCME (2001c) Criteria 1 as the linearity for single compounds was found to be within 10% (greater than 0.9 R^2 value) and within 15% (greater than 0.85 R^2 value) for each carbon range (F2, F3, and F4) of the product such as motor oil. Table 4.4 provides the RF values obtained for each n-alkane using Equation (1) described in Section 3.2.3.2. A detailed calculation for the individual and average RF is provided in Appendix A. Table 4.4 clearly shows that the individual n-alkane RFs are within 10% of each other as required by the Criteria 2. Table 4.4 provides the RF value of nC_{50} used as a response factor standard. The nC_{50} RF value lies within 70% of RFavg thereby meeting the calibration Criteria 2 as per CCME (2002-c). RFavg is the average of the RFs obtained for each of the n-alkanes using Equation (2) provided in Section 3.2.3.2. Detailed calculation is provided in Appendix A.

Figure 4.15 shows the chromatogram of 5000 ppm motor oil calibration standard. In order to check the linearity of the calibrated carbon ranges, the peak areas for individual carbon ranges of the motor oil calibration standards are calculated.

Table 4.2: Linearity of single compounds (n-alkanes) obtained using calibration Method 1 and Method 2

n-ALKANE	R^2	REQUIRED R^2 (AS PER CCME CRITERIA 1)
METHOD 1		
nC_{10}	0.9969	
nC_{16}	0.9990	> 0.9
nC_{34}	0.9987	
METHOD 2		
nC_{10}	0.9666	
nC_{16}	0.9882	> 0.9
nC_{34}	0.9999	

Table 4.3: Linearity of F2, F3, and F4 fractions of motor oil calibration standards obtained using calibration Method 1 and Method 2

MOTOR OIL CARBON RANGE	R^2	REQUIRED R^2 (AS PER CCME CRITERIA 1)
METHOD 1		
F2 (nC_{10}-nC_{16})	0.9691	
F3 (nC_{16}-nC_{34})	0.9910	> 0.85
F4 (nC_{34}-nC_{50})	0.9398	
METHOD 2		
F2 (nC_{10}-nC_{16})	0.9945	
F3 (nC_{16}-nC_{34})	0.9982	> 0.85
F4 (nC_{34}-nC_{50})	0.9513	

Table 4.4: RF values of n-alkanes obtained by running calibration standards

n-Alkane	RFs	Average RF	Standard Deviation	RSD	Criteria
METHOD 1					
nC_{10}	3403906176	3564859483	206979542	**5.8%**	**<10%**
nC_{16}	3492329420				
nC_{34}	3798342853				
nC_{50}	4447666667				**within 70% of RFavg**
METHOD 2					
nC_{10}	1659832155	1709270793	82540652	**4.8%**	**<10%**
nC_{16}	1663422236				
nC_{34}	1804557988				
nC_{50}	1551887324				**within 70% of RFavg**

This is obtained by summing the peak areas from 2.7 to 7.9 minutes (retention time window for nC_{10}-nC_{16} or F2), 7.9 to 17.4 minutes (retention time window for nC_{16}-nC_{34} or F3), and 17.4 to 21.8 minutes (retention time window for nC_{34} to nC_{50} or F4) for Method 1 as specified in Table 4.1. The peak areas are summed using the "Group Peaks" (GR) function of the Star Chromatography data handling software. This feature allows all peaks in the respective retention time windows to be reported as a single peak with the separation code 'GR' and a retention time set to the midpoint of the window.

A similar procedure was followed using Method 2 when the GC was recalibrated. Figure 4.15 shows that motor oil mainly contains F3 fraction (nC_{16}-nC_{34}) of PHCs. The lower values of the linear correlation coefficients obtained for F2 and F4 fractions in Table 4.3 are explained by the motor oil chromatogram shown in Figure 4.15.

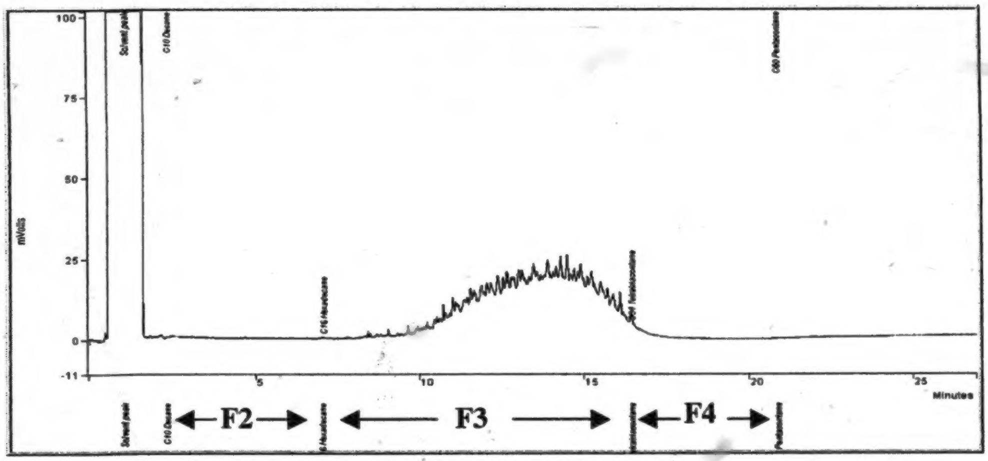


Figure 4.15: Chromatogram of 5000 ppm motor oil calibration standard

4.2.3 GC Method Validation

As mentioned in section 3.2.3.2, to check the stability of the calibration curve, GC response for variations in the chromatogram detection and sensitivities was monitored by injecting mid-point calibration standard (1000 ppm) for most of the batch runs and 5000-ppm calibration standard for some of the batches of GC sample injections. These standards contained mixtures of appropriate amounts of nC_{10}, nC_{16} and nC_{50} alkanes. Due to the consistency of the results obtained by the calibration verification standard and hence the stability of calibration curve, the calibration verification was practiced after every 2-3 batches of samples. Table 4.5 shows the results of the injections of these calibration standards. Since, the results of GC analyses were obtained as group areas for F2, F3 and F4 fraction, the same group areas obtained from the injections of calibration verification standards were then compared with the areas obtained during the time of calibration. The total areas obtained for the old calibration standard and the new calibration verification standard were compared to calculate the % drift (see Appendix C for raw data of verification calibration standards). GC/FID operation was checked and restored to normal if considerable deviations of >20% (CCME, 2001-c) from the curve were detected. The % drifts or deviations in this work ranged from –18% to +18%, which were still <20%. The average % drift obtained for all the injections of 1000 ppm and 5000 ppm verification standards was found to be not more than 3% (Table 4.5) indicating that the averages were quite accurate. In order to avoid high % drifts, GC injector septa, and injector liner were replaced at regular intervals, non-maintenance of which results in deviations from the calibration curve.

Table 4.5: GC analyses for calibration verification standards

Theoretical concentrations of calibration standard (ppm)	Corresponding area obtained for the calibration standard	Measured areas from all injections			% Average Drift from expected
		Mean	Standard deviation	RSD (%)	
1000	3799230	3571156 (11)	323248	9	2
5000	11868109	12265923 (5)	1267745	10	3

Pure toluene injections were done as blank injections to clean the column between samples from each run, and to check false-positives due to sample carry-over in the GC column. Gas supply cylinders with lower than desired pressures may affect the carrier and make up gas flow through the GC column, thereby resulting in deviations. Gas cylinders were also changed as required in order to avoid any deviations in the results. Table 4.5 shows that the relative standard deviations obtained for the GC verification ranged from 9 to 10%, which are much less than those obtained for the actual soil samples injections.

Samples of spiked soils, and blank samples were also sent to Enviro-test, a commercial independent laboratory. This was done to confirm the efficacy and efficiency of the laboratory protocols and analysis developed in this work. Table 4.6 shows the comparison of the samples analyses done in-house and sent to a commercial laboratory (Enviro-Test Laboratory, Edmonton, Alberta). In-house GC injections and calculations show that clean flare pit soil, which was collected at a few meters distance away from the flare pit site 1 contains less than 0.002% HCs. Enviro-Test also reported the value below their detection limit of 0.0005% (5 mg/kg).

To investigate any positive errors due to the method, method blanks were run, which were empty thimbles without the soil sample that were soxhlet extracted and quantified by GC thereafter. The average value reported was 0.004%, which is negligibly small. Also, the values reported for the GC injections of clean sand were found to be within 0.002% as obtained in-house and by Enviro-Test laboratory. The values reported for method blank, clean flare pit soil, and clean sand being negligible shows that no false positive values are being added to the measured petroleum hydrocarbon content,

Table 4.6: Sample analyses results obtained in the lab and in the commercial lab

	In House	Enviro-Test commercial laboratory
Solvent extraction method blank	<.004% (n=2)	
Clean flare pit sand	0.002% (n=2)	<0.0005% (n=1)
Clean sand	0.002% (n=2)	0.002% (n=2)
Spiked sand (4.06%)	3.90% (n=2)	3.2% (n=1)
Spiked sand (4.69%)	4.19% (n=3, SD= 0.58%)	
Spiked sand (2.99%)	2.21% (n=3, SD= 0.77%)	

n=number of sub-samples used for analyses; SD = Standard deviation of results

and that the clean sand samples do not contain PHCs. Spiked sand at 4.06% was also prepared by homogenizing 9.75 g of weathered diesel oil with 240.38 g of clean sand, two sub-samples of which were immediately solvent extracted, and one was sent to Enviro-Test Laboratory In-house analyses of the spiked sand gave an average PHC content value of 3.9%, while Enviro-Test (8-9 days later) returned result showed an average PHC content of 3.2%. The lower value of PHCs reported by Enviro-Test could be accounted by the volatilization of lighter hydrocarbons in the spiked soil as a result of the analyses turnaround time of about 7-8 days. Two more sand samples were spiked at 4.69% and 2.99% and were analyzed in-house only. The lower value of the results

(4.19% and 2.21%) than expected suggest that lighter HCs might have been volatilized during the sample handling and preparation steps for soxhlet extraction.

In summary, the results obtained by running method blanks, clean flare pit soil, clean sand were negligible. The results for spiked sand although lower, were close to the expected. In addition, analyses of replicated SC CO_2 extractions, and GC analyses of all the samples verify the consistency and reliability of results. Thus, in-house analyses should be accepted as correct

4.2.4 Extraction Efficiency

The following samples were analyzed by GC/FID for PHC content:

1. Untreated or raw FP 1
2. Untreated or raw FP 2
3. Treated or SC CO_2 extracted FP 1
4. Treated or SC CO_2 extracted FP 2

The results of these analyses allowed the calculation of extraction efficiencies for the experiments conducted. Figure 4.16 show the chromatograms of raw contaminated FP 1 and FP 2, indicating the three groups or the F2, F3 and F4 fractions of PHCs present in the soil. These individual areas obtained as three group areas were used in calculations of the individual PHC concentrations of F2, F3 and F4 fractions present in the soil sample and hence the total extraction efficiency.

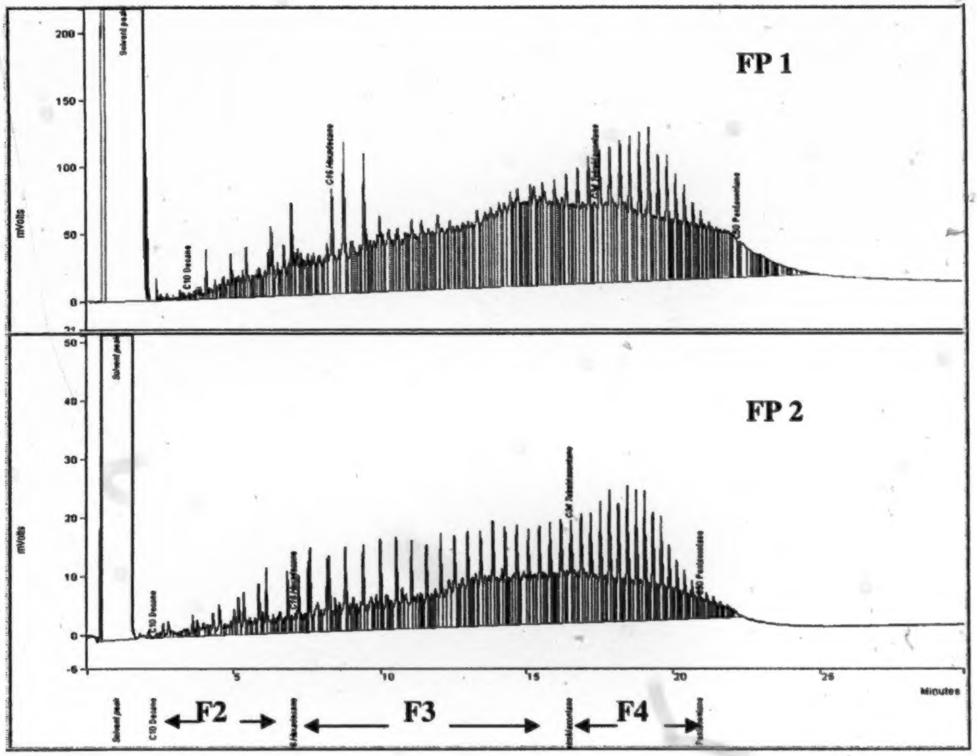


Figure 4.16: Chromatograms of contaminated FP 1 (top) and FP 2 (bottom) showing PHC fractions F2, F3, and F4

The results of this work are presented in Tables 4.7 to 4.9. Table 4.7 shows the PHCs results obtained for untreated FP 1 and for SFE treated flare pit soil at various extraction pressures ranging from 11.0 MPa to 24.1 MPa and at 40°C. Table 4.8 provides PHCs results for FP 1, obtained at 25°C, 60°C and 80°C for extraction pressures ranging 12.4 MPa to 15.2 MPa. Similarly, Table 4.9 shows PHCs results obtained for untreated FP 2 and for SFE treated flare pit soil at various extraction pressures ranging from 13.8 MPa to 24.1 MPa and at 40°C.

The reported value of total petroleum hydrocarbon (TPH) content of 31248 mg/kg (or 3.1%) in Table 4.7 for raw untreated FP 1 is the value obtained from in-house analyses (in lab). However, a TPH value of 31774 mg/kg obtained by averaging the analyses values obtained from in-house PHC analysis (31248 mg/kg) and from commercial lab analysis (32300 mg/kg), was used in calculating the extraction efficiencies at all SC CO_2 extraction conditions for FP 1. The reported value of total petroleum hydrocarbon content of 105200 mg/kg in Table 4.8 for untreated FP 2 is the average of the PHC content values obtained from in-house analyses (in lab), while the number used for calculating the extraction efficiencies of PHCs from FP 2 at various SC CO_2 conditions is the average of in-house analyses (105200 mg/kg) and the total PHC content data obtained by two other external laboratories (115500 mg/kg, 117000 mg/kg). Thus, a total PHC content value of 112600 mg/kg was used for calculating the extraction efficiencies at all SC CO_2 extraction conditions for FP 2. Figure 4.17 shows a sample of resultant chromatogram of the FP 1 prior to and following SC CO_2 extraction at 24.1 MPa and 40°C.

Sample calculations of the total PHC content that includes F2, F3 and F4 PHC fractions present in the untreated and treated soil are presented in Appendix A. The results presented in Table 4.7, Table 4.8 and Table 4.9 are the results obtained from averaging the data for 9 individual GC injections for three sub-samples ran at all extraction conditions. In order to reduce the variability in the final results, three sub-samples of the soil from each experiment were collected and prepared for GC/FID analysis. Preparation of each of the three sub-samples yielded an extract that was diluted and injected into the GC/FID three times.

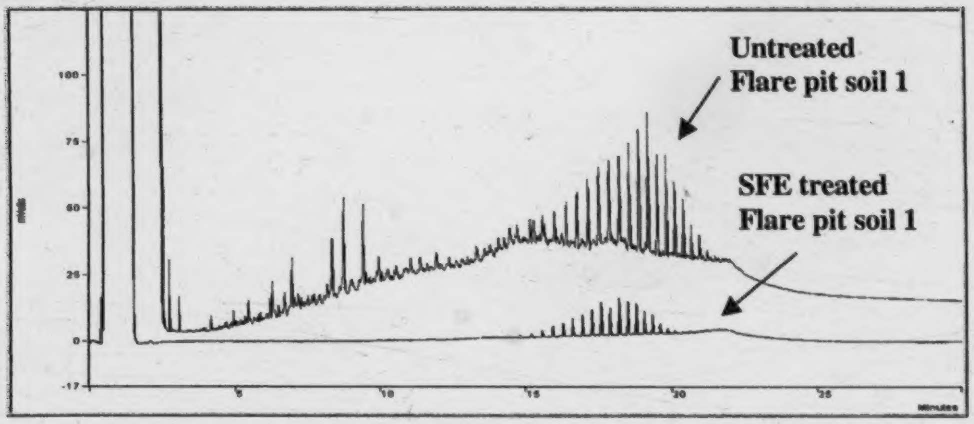


Figure 4.17: Chromatograms of untreated real FP 1 and SFE treated flare pit soil at 24.1MPa and 40°C

Thus, each experiment resulted in an average of nine injections. In addition, each experiment was run in duplicate to ensure reproducibility. It should be noted that in Table 4.7, the extraction experiments performed at pressures of 13.8 MPa and 15.2 MPa and at a temperature of 40°C were run in triplicates. A third experiment was added in both cases since the extraction efficiencies of the two first runs appeared quite different (see Table 4.7). Observations made from the plots of the pressure data obtained at these two extraction conditions (Run 1 at 13.8 MPa and Run 2 at 15.2 MPa) showed large fluctuations in the pressure transducer reading, which is the pressure in the vessel. This suggests that the low extraction efficiencies obtained for these two extraction runs might have occurred due to pressure fluctuations in the vessel.

Table 4.7: Petroleum Hydrocarbon extraction results for FP 1 at 40°C

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	SC CO_2 Density (g/mL)	Mean (mg/kg)	Number of sub-samples	Number of injections	Standard deviation (mg/kg)	RSD (%)	Extraction efficiency (%)
Raw FP 1	N/A	N/A	N/A	31200	5	15	7719	25	N/A
10	11.0	40	0.68	9504	3	9	6766	71	70
	11.0	40	0.68	9869	3	9	6344	64	69
	12.4	40	0.73	9188	3	9	2089	24	71
	12.4	40	0.73	8794	3	9	1667	18	72
	13.8	40	0.76	9510	2	6	1295	12	70
	13.8	40	0.76	5997	3	9	2837	47	81
	13.8	40	0.76	5499	3	9	826	15	83
	15.2	40	0.78	5405	3	9	2355	44	83
	15.2	40	0.78	8386	3	9	1531	18	74
	15.2	40	0.78	4317	3	9	1424	36	86
	20.7	40	0.85	3753	3	9	770	21	88
	20.7	40	0.85	4484	3	9	1242	28	86
	24.1	40	0.87	3362	3	9	381	11	89
	24.1	40	0.87	3603	3	9	750	21	89
20	15.2	40	0.78	7297	3	9	4006	55	77
	15.2	40	0.78	7603	3	9	4774	63	76
5	15.2	40	0.78	6980	3	9	4479	64	78
	15.2	40	0.78	9331	3	9	3536	38	71
1	15.2	40	0.78	7180	3	9	5456	76	77
	15.2	40	0.78	7577	3	9	3558	49	76

* density calculated using Lemmon et al. (2003)

Table 4.8: Petroleum Hydrocarbon extraction results for FP 1 at 25°C, 60°C, and 80°C

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	SC CO_2 Density (g/mL)	Mean (mg/kg)	Number of sub-samples	Number of injections	Standard deviation (mg/kg)	RSD (%)	Extraction efficiency (%)
10	15.2	25	0.88	12500	3	9	3968	32	61
	12.4	60	0.47	16814	3	9	3736	22	47
	12.4	60	0.47	17943	3	9	3920	22	44
	13.1	60	0.51	15654	3	9	2510	16	51
	13.1	60	0.51	18848	3	9	1924	10	41
	13.8	60	0.55	13902	3	6	8777	49	56
	15.2	60	0.61	9162	3	9	5248	57	71
	15.2	60	0.61	6169	3	9	1220	22	81
	15.2	80	0.43	19119	3	9	8143	43	40
	15.2	80	0.43	16377	3	9	7345	45	48

Table 4.9: **Petroleum Hydrocarbon extraction results for FP 2 at 40°C**

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	SC CO_2 Density (g/mL)	Mean (mg/kg)	Number of sub-samples	Number of injections	Standard deviation (mg/kg)	RSD (%)	Extraction efficiency (%)
Raw FP 2	N/A	N/A	N/A	105200	4	12	5866	6	N/A
10	13.8	40	0.76	45086	3	9	7958	14	60
	13.8	40	0.76	47659	3	9	11536	18	58
	14.8	40	0.78	36864	3	9	17430	51	67
	14.8	40	0.78	40310	3	9	20001	54	64
	24.1	40	0.87	22591	3	9	5783	26	80
	24.1	40	0.87	24326	3	9	7749	35	78

4.2.4.1 Extraction efficiency for specific PHC Fractions

The extraction efficiencies presented in Table 4.10 to Table 4.12 were calculated using the average PHC content values of 31800 mg/kg and 112600 mg/kg for raw untreated FP 1 and for FP 2, respectively. The extraction efficiency therefore indicates how successfully the SC CO_2 extraction was able to reduce PHCs from 31800 mg/kg and 112600 mg/kg from FP 1 and 2, respectively. The aim of this work was to bring the PHCs level present in the SFE treated soil below CCME soil quality guidelines for PHC contaminated soil (CCME 2001b) as mentioned in Section 3.1.1 (Table 3.2). The laboratory-scale efficiencies and extraction conditions established in Table 4.10 to Table 4.12 also show the % removal of individual F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}), and F4 (nC_{34}-nC_{50}) fraction of PHCs present in the SFE treated flare pit soils obtained at various extraction conditions. It was observed that the mean PHC content values obtained at pressure conditions from 13.8 MPa to 24.1 MPa at 40°C are not significantly different from each other (based on ANOVA analysis performed at 95% confidence interval, discussed in detail in Section 4.3). However, an increase in the removal of F4 fraction of PHCs from FP 1 with an increase in pressure at 40°C helped in meeting the regulatory criteria for the PHC fractions levels in the contaminated soils (CCME 2001a).

Tables 4.10 to 4.12 provide three different methods for calculating the extraction efficiencies for both FP 1 and FP 2. Method A shows the extraction efficiency values taking into consideration that 9.05% moisture (as determined in house) was present in raw untreated FP 1 (Tables 4.10 and 4.11), and 8.26% moisture was present in the raw untreated FP 2 (Table 4.12), and that this moisture was still present in the SFE treated soil. On the other hand, Method B shows the extraction efficiency values assuming that all of the moisture was extracted during the SC CO_2 extraction runs, i.e. no moisture is present in the SFE treated soils. According to the method for the determination of moisture present in soil samples as described by CCME (2001c), some of the lighter HCs are volatilized during the moisture content determination. The moisture content for the present soils as stated above, includes some unknown percentage of the lighter end HCs that might have been volatilized in the oven during the drying process for moisture content determination. This loss of HCs along with water leads to a lighter weight determination of the sample matrix than the actual weight and thus, may account for the higher moisture content values.

Due to the uncertainty in the moisture content of the untreated soils and due to the uncertainty in the amount of water extracted during the experiment, the moisture content of the treated samples was assumed to be between 0% and 9% (for FP 1) or 0% and 8% (for FP 2). Extraction efficiencies were therefore calculated using both the maximum moisture contents of the treated soil (i.e. 9% for FP 1 and 8% for FP 2, see Method A values in Tables 4.10 to 4.12) and the minimum moisture content values (0% for both soils, see Method B in Tables 4.10 to 4.12). This window covers any errors in reporting the extraction efficiencies due to loss of water during the extraction runs.

Both calculation Methods A and B showed similar results in terms of extraction efficiency. Thus, it was assumed that no (or negligible) amount of water was extracted during the extractions performed in this work. This observation was confirmed by determining the solubility of water in SC CO_2 at each extraction condition of temperature and pressure, and converting it into grams of water that would be extracted at those conditions assuming solubility was reached. The solubility of water at all extraction conditions were obtained using a solubility calculator developed by Warren Stiver and Greg Rampley from the University of Guelph (Stiver and Rampley 2001). Table D-1 in Appendix D shows the results in grams of water that might have been extracted if the solubility of water was reached at those extraction conditions. The results show that the mass of water that might have been extracted at these extraction conditions is negligible, and that this amount does not considerably change the extraction efficiency of the PHCs if the moisture content is assumed not to change with the extraction.

The third extraction efficiency calculated by Method C (see Tables 4.10 to 4.12) represent the expected % extraction of PHCs based on the mass of HCs collected during SC CO_2 extractions (see Appendix E for sample calculation). This mass of HCs also includes the mass of HCs collected during bypassing CO_2 through the line downstream of the vessel. The mass collected in the bypass vial ranged on an average from 0.1g to 0.2 g of the total HCs collected. Table 4.10 shows that the value of expected extraction efficiency is quite uncertain as it varies from one extraction run to another, performed at the same SC CO_2 extraction conditions.

Table 4.10: **Petroleum hydrocarbon extraction results for FP 1 at 40°C**

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	Density of SC CO_2 (g/mL)	Extraction efficiency (%)			F2 removal (%)	F3 removal (%)	F4 removal (%)
				Method A	Method B	Method C			
10	11.0	40	0.68	70	73	104	91	87	36
	11.0	40	0.68	69	72	90	95	85	36
	12.4	40	0.73	71	74	91	98	81	48
	12.4	40	0.73	72	75	112	98	82	49
	13.8	40	0.76	70	72	98	99	88	33
	13.8	40	0.76	81	83	78	99	90	62
	13.8	40	0.76	83	84	72	99	96	57
	15.2	40	0.78	83	85	130	99	92	64
	15.2	40	0.78	74	76	112	98	85	48
	15.2	40	0.78	86	88	89	93	97	68
	20.7	40	0.85	88	89	124	99	97	71
	20.7	40	0.85	86	87	107	96	95	69
	24.1	40	0.87	89	90	109	100	98	73
	24.1	40	0.87	89	90	112	99	98	72
20	15.2	40	0.78	77	79	209	98	95	41
	15.2	40	0.78	76	77	120	100	94	40
5	15.2	40	0.78	78	80	98	98	95	45
	15.2	40	0.78	71	73	58	96	88	35
1	15.2	40	0.78	77	79	42	96	88	55
	15.2	40	0.78	76	78	53	98	91	46

A - assuming 9% moisture content
B - assuming 0% moisture content
C - based on mass of HCs collected

Table 4.11: Petroleum hydrocarbon extraction results for FP 1 at 60°C and 80°C

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	Density of SC CO_2 (g/mL)	Extraction efficiency (%)			F2 removal (%)	F3 removal (%)	F4 removal (%)
				Method A	Method B	Method C			
10	15.2	25	0.88	61	64	34	94	65	48
	12.4	60	0.47	47	52	60	98	44	38
	12.4	60	0.47	44	49	43	98	38	36
	13.1	60	0.51	51	55	65	99	50	38
	13.1	60	0.51	41	46	60	99	43	20
	13.8	60	0.55	56	61	63	95	54	52
	15.2	60	0.61	71	74	101	99	80	50
	15.2	60	0.61	81	82	74	99	91	58
	15.2	80	0.43	40	45	93	98	48	10
	15.2	80	0.43	48	53	124	99	55	23

A - assuming 9% moisture content B - assuming 0% moisture content C - based on mass of HCs collected

Table 4.12: Petroleum hydrocarbon extraction results for FP 2 at 40°C

SC CO_2 flow rate (mL/min)	Pressure (MPa)	Temperature (°C)	Density of SC CO_2 (g/mL)	Extraction efficiency (%)			F2 removal (%)	F3 removal (%)	F4 removal (%)
				Method A	Method B	Method C			
10	13.8	40	0.76	60	63	62	99	73	17
	13.8	40	0.76	58	61	54	96	65	26
	14.8	40	0.78	67	70	55	100	81	27
	14.8	40	0.78	64	67	49	99	72	34
	24.1	40	0.87	80	82	82	99	95	43
	24.1	40	0.87	78	82	82	98	94	48

A - assuming 9% moisture content B - assuming 0% moisture content C - based on mass of HCs collected

Table 4.10 suggests that an increase in pressure increased the mass of PHCs collected during the extraction and hence, increased the calculated extraction efficiency. The inconsistency in the expected efficiency value (Method C) from the actual value obtained from GC/FID analysis suggests that higher pressures and higher flowrates might help in the extraction of compounds other than PHCs that were evidently not analyzed by GC. Extraction efficiencies greater than 100% may also suggest that SFE is a better solvent extraction process than Soxhlet extraction for extraction of PHCs from flare pit soils. This is because, the values of PHC content obtained from soxhlet extracted untreated flare pit soils were compared to mass of PHCs collected during SFE. Thus, higher mass of PHCs collected (therefore, >100% extraction efficiency) during SFE suggests that SFE is more effective than Soxhlet extraction.

The laboratory-scale PHC extraction efficiencies and optimal conditions established by this work would provide data and therefore the basis to develop a pilot scale design for treatment of biorecalcitrant petroleum hydrocarbon contaminated soils, which are otherwise both time-consuming and costly. The effects of various factors such as the extraction temperature, pressure, SCF density, CO_2 flowrate, and soil type on the extraction efficiency are discussed in the following sections.

4.2.4.2 Effect of Temperature

It is known from the literature that temperature affects the extraction efficiencies in two ways. First, an increase in temperature can increase the amount of PHCs extracted (and hence the extraction efficiency) by increasing the volatility of the PHCs or by increasing the rate of desorption of the PHCs from the soil. Second, an increase in temperature can decrease the amount of PHCs extracted by affecting the SC CO_2 density. As the temperature increases (at constant pressure), the SC CO_2 density decreases becoming more gas-like and resulting in a lower PHC solubility and thus a lower extraction efficiency. The balance of both the above mentioned factors determine the overall effect of temperature on the extraction efficiency.

Hwang et al. (1995) in their study indicated that the extraction behaviour of a mixture of HCs from crude oil appeared independent of temperature in the vicinity of the critical temperature of CO_2 (31°C). A significant reduction in the amount of extracted oil was also observed at a temperature (66°C) well above the critical temperature (Hwang et al. 1995). Similar observations were made in this work. Figure 4.18 shows the trend of decrease in extraction efficiency with an increase in temperature, where an increase in temperature from 40°C to 80°C at a constant pressure of 15.2 MPa resulted in a decrease in the extraction efficiency of PHCs from FP 1, from 86% to 41%. Since extraction efficiencies in Figure 4.18 appear to be decreasing with an increase in temperature, it may be concluded that, over the temperature range studied, the extraction of PHCs from FP 1 is more strongly affected by the supercritical fluid density rather than by contaminant volatility or desorption kinetics. Statistical analysis of the results showed that an increase in temperature at a constant pressure significantly increased the extraction efficiency. This finding is consistent with that of Hwang et al. (1995) who also found that, for the SC CO_2 extraction of complex hydrocarbon mixtures, the extraction efficiency is governed by the supercritical fluid density.

The effect of temperatures higher than 80°C could not be investigated due to the inability of the water bath to achieve temperatures higher than 100°C (boiling point of water). Using another circulating fluid other than water (oil for example) would enable the investigation of extractions at temperatures higher than 80°C.

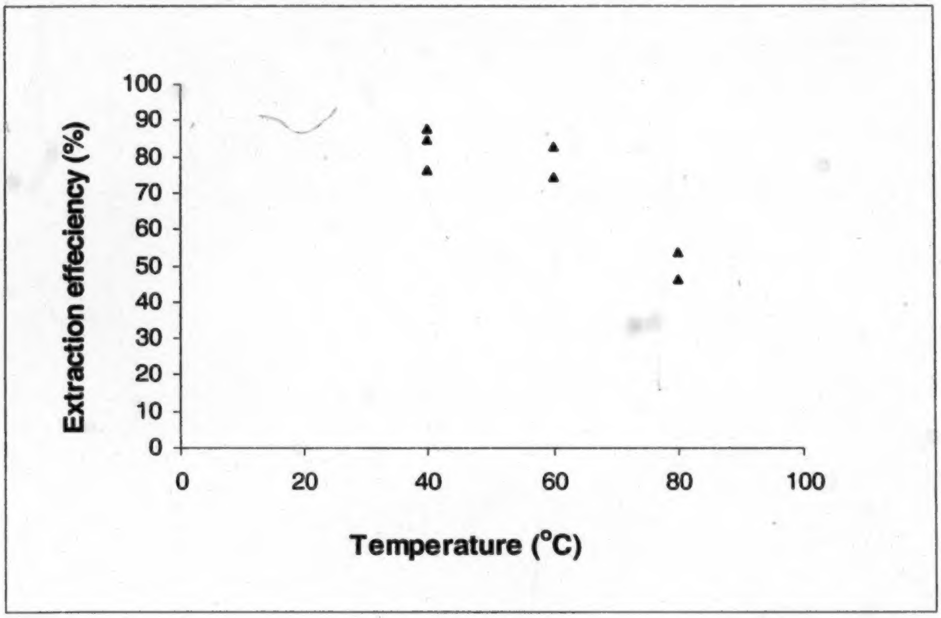


Figure 4.18 : Effect of temperature at constant pressure (15.2 MPa)

4.2.4.3 Effect of Pressure

Extractions were carried out at pressures ranging from 11.0 MPa to 24.1 MPa. The extraction efficiencies given in Tables 4.10 to 4.12 show that, within the range of conditions studied here, as the pressure increases at a constant temperature, the extraction efficiency increases. The highest extraction efficiency was obtained at 40°C and 24.1 MPa, conditions that yielded the highest supercritical fluid density (0.87 g/mL). At these conditions, GC analyses of the SFE treated flare pit soil samples indicate that an average of 89% of total PHCs were extracted from FP 1 and 80% of the total PHCs were extracted from FP 2. Figure 4.19 shows the trend of increasing extraction efficiency with increasing pressure at constant temperatures. For example, the extraction efficiency increased from 69% to 89% with an increase in pressure from 11.0 MPa to 24.1 MPa at 40°C.

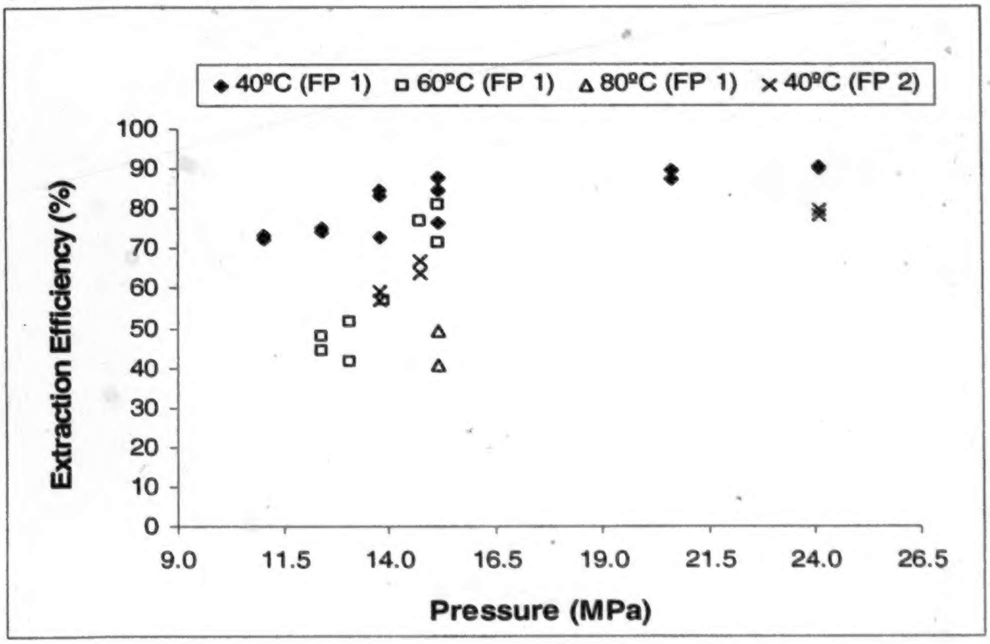


Figure 4.19: **Effect of pressure at different temperatures**

Many authors have found that as the pressure increases, the extraction efficiency increases. This behavior was also observed by Rudzinski and Aminabhavi (2000) who found that crude oil extraction increased with an increase in pressure from 7.6 to 17.2

MPa at 38°C. The increase in extraction efficiency with an increase in pressure at a fixed temperature is related to the increase in supercritical fluid density and that an increase in density results in an increase in extraction efficiency (Hwang et al. 1995). This effect of supercritical fluid density will be discussed further in the following section.

The extraction efficiencies obtained at extraction conditions ranging from 13.8 MPa to 24.1 MPa and at 40°C, ranged from 81% to 89% with HCs ranging from 6000 mg/kg to 3360 mg/kg (see Table 4.7). To verify if the means of the PHC content ranging from 13.8 MPa to 24.1 MPa at 40°C (extraction efficiency ranging between 81% to 89%) were different from each other, an analysis of variance (ANOVA) was performed at a significance level (p) of ≤5%. The ANOVA analysis of the mean PHC content obtained at the extraction conditions ranging from 13.8 MPa to 24.1 MPa at 40°C indicated that no significant difference appears between the PHC contents obtained at these conditions (see Appendix F1). ANOVA analysis was also carried out on the mean PHC contents obtained at the extractions performed at 60°C and at pressures ranging from 13.8 MPa to 15.2 MPa, for FP 1 (see Table 4.8). Similarly, ANOVA analysis at a significance level (p) of ≤5% for FP 2 was performed at 40°C and at pressures ranging from 13.8 MPa to 24.1 MPa (see Table 4.9). Results from both the analyses indicated that the SFE extracted PHC content results were significantly different from one SC CO_2 extraction condition to another, for FP 1 at 60°C, and FP 2 at 40°C (see Appendix F2). Thus, from the above-mentioned results, it can be interpreted that an increase in pressure at constant temperature significantly affects the extraction efficiency.

The effect of pressure on the extraction efficiencies for each of the individual PHC fractions (F2, F3 and F4, as specified by CCME (2001a) was also investigated.

Figure 4.20 and Figure 4.21, shows the effect on % removal of F2 (nC_{10}-nC_{16}), F3 (nC_{16}-nC_{34}), and F4 (nC_{34}-nC_{50}) fractions of PHCs with an increase in pressure for FP 1 and FP 2, respectively. An increase in pressure played an important role in the removal of PHC fractions specifically the F4 fraction (nC_{34}-nC_{50}). As illustrated in Figure 4.20, for most of the extractions performed on FP 1 at 40°C, 98% to 100% of the F2 fraction of PHCs was extracted. For the F3 fraction of FP 1, the extraction efficiencies ranged from 87% to 98% at 40°C. For the F4 fraction of FP 1, an increase in pressure from 11.0 MPa to 24.1 MPa increased the extraction efficiency from 36% to 73%, respectively. In the case of FP 2, the extraction efficiencies for the F2, F3 and F4 fractions increased from 96 to 100%, 65 to 95% and 17 to 48%, respectively, with an increase in pressure from 13.8 MPa to 24.1 MPa at 40°C (as illustrated in Figure 4.21).

These results show that, for both soils, the F2 fraction was removed to a greater extent than both the F3 and F4 fractions and the F4 fraction was the most difficult to remove. Based on the Federal Soil Quality Guidelines for coarse-grained surface soil in an industrial area (CCME 2001b), the % removals greater than 76%, 90% and 69% for F2, F3 and F4 fraction respectively should be obtained for FP 1. Similarly, % removals for F2, F3, and F4 fractions should be greater than 82%, 92%, and 71% respectively for FP 2 to meet the soil quality criteria for fine- grained sub-soil (CCME 2001a). These values are in accordance with the PHC content values required for each individual PHC fraction to meet the CCME criteria for industrial soil as illustrated in Table 2.1.

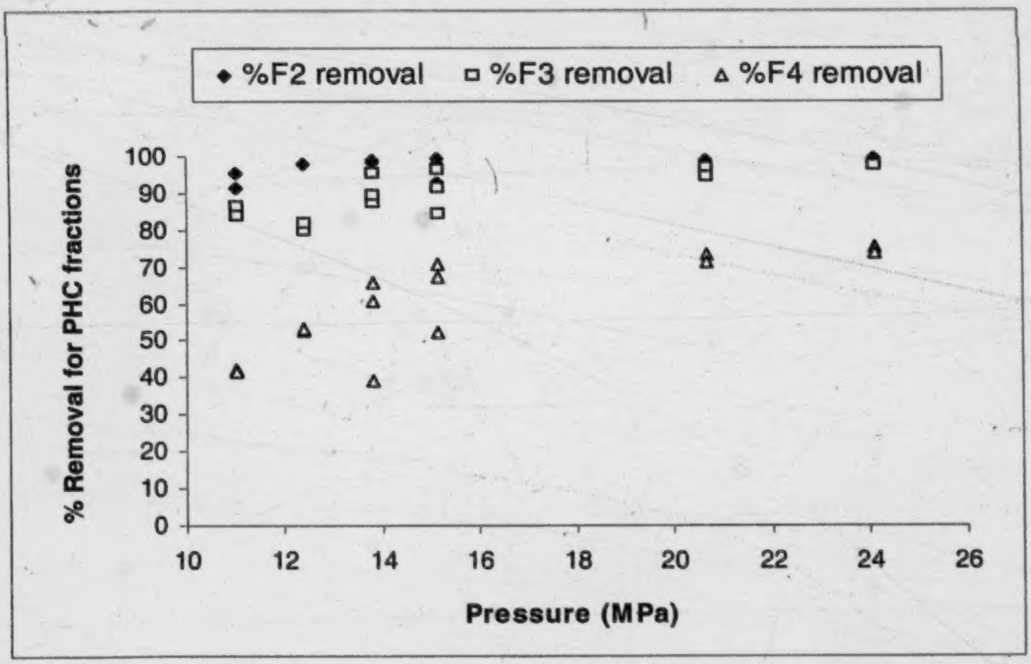


Figure 4.20: Petroleum hydrocarbon fraction removal (%) for FP 1 at 40°C

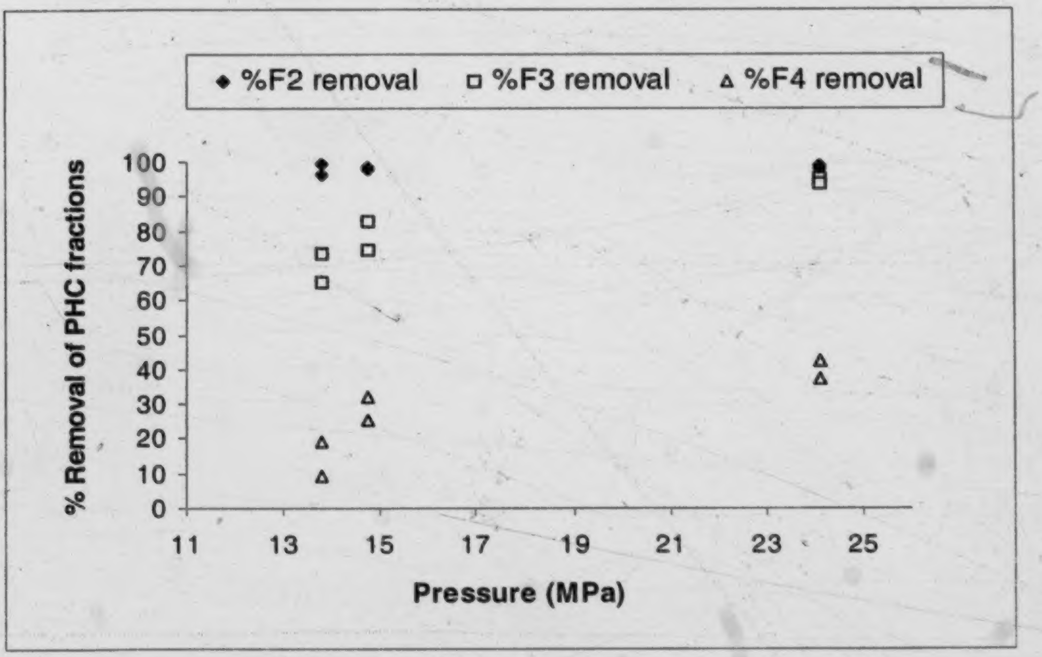


Figure 4.21: Petroleum hydrocarbon fraction removal (%) for FP 2 at 40°C

Thus, it was observed that both the F2 and F3 fractions of PHCs in the treated FP 1 were able to meet regulatory guidelines at extraction conditions of 15.2 MPa and above. The F4 fraction of FP 1 was able to meet regulatory guidelines after treatment at 24.1 MPa and 40°C. Similarly, for FP 2, the F2 fraction met regulatory guidelines for all extraction conditions tested while the F3 fraction met the regulatory guidelines at 24.1 MPa. The F4 fraction of FP 2 was not able to meet the regulatory guidelines after treatment at the pressure and temperature conditions tested. In order to determine whether the F4 fraction can be better extracted, more extractions at higher pressures need to be conducted.

4.2.4.4 Effect of Density

Density is a function of both temperature and pressure. Figure 4.22 shows a plot of the extraction efficiency as a function of SC CO_2 density for FP 1 and FP 2 at various temperatures. The SC CO_2 densities for the pressure and temperature conditions used in this work were determined using the on-line National Institute of Standard and Technology (NIST) Chemistry WebBook (Lemmon et al. 2003).

An increase in the extraction efficiency (from 44% to 81%) is observed at 60°C with an increase in densities from 0.48 to 0.61 g/mL, whereas the extraction efficiencies at 40°C increased (from 69% to 83%) with an increase in density from 0.68 to 0.78 g/mL but remained relatively constant (between 83% to 89%) with an increase in density ranging from 0.78 g/mL to 0.87 g/mL. Similarly, an increase in the extraction efficiency from 58% to 80% was observed with an increase in density from 0.76 to 0.87 g/mL for

FP 2 at 40°C. Thus, an increase in density at a particular temperature resulted in an increase in the extraction efficiency, especially at the temperature (40°C) close to the critical temperature of SC CO_2 (31°C).

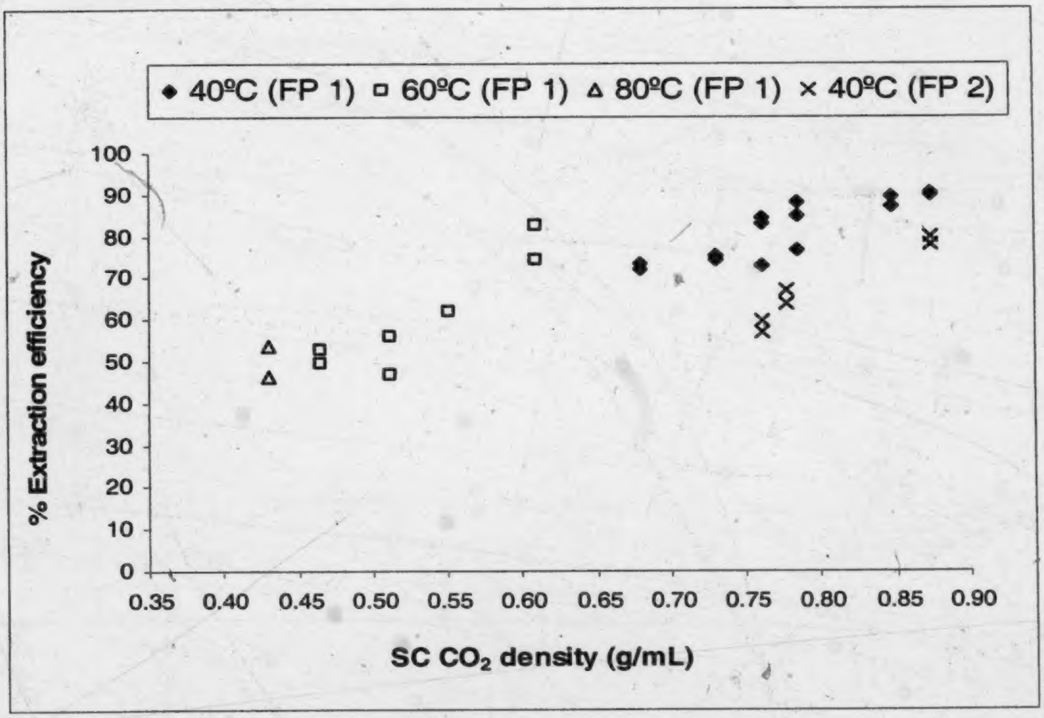


Figure 4.22: Effect of SC CO_2 density on extraction efficiencies

Table 4.12 shows that at 40°C, an increase in extraction pressure from 11.0 MPa to 24.1 MPa indicated an increase in the SC CO_2 density from 0.68 g/mL to 0.87 g/mL (see Figure 4.22), which showed an increase in the extraction efficiency of FP 1 from 69% to 89%. A similar trend of an increase in extraction efficiency was observed for FP 2 (see Figure 4.22), where an increase in density of 0.78 to 0.87 g/mL (from 14.8 MPa to 24.1 MPa) resulted in a 14% increase in the extraction efficiency of FP 2 (from 64% to 80%).

This trend of increase in extraction efficiency with SCF density was also observed at a temperature of 60°C (see Figure 4.22). However, these extraction efficiencies were lower in comparison to those obtained at similar pressure conditions and constant temperature of 40°C, a temperature in the vicinity of the critical temperature of CO_2 (31°C). Hwang et al. (1995) indicated that the extraction behaviour appeared independent of temperature in the vicinity of the critical temperature (31°C) of CO_2. It was also observed that well above the critical temperature (at 66°C), the amount of oil extracted was significantly reduced (Hwang et al. 1995). However, at a higher temperature of 60°C in the current work, the change in density from 0.47 to 0.61 g/mL caused the extraction efficiency to almost double its value (from 44% to 81%) obtained at 0.47 g/mL (see Figure 4.22). It is to be noted that no two extraction run results are similar for the SC CO_2 extractions performed at 60°C at different pressures ranging from 12.4 MPa to 15.2 MPa (see Table 4.10 and Figure 4.22). This may be due to the combined effect of the heterogeneous nature of the soil and the decrease in density observed at higher temperatures (60°C and 80°C) than at 40°C (see Tables 4.10 to 4.12). As a result of a decrease in density, the solubility of the contaminant (in this case PHCs) in supercritical fluid decreases, thereby decreasing the extraction efficiency. There is a need to perform more experiments at 60°C, so as to be definite of the extraction efficiencies obtained (see Table 4.11). The variability of the results obtained at 60°C is discussed in detail in Section 4.3.

Thus, relatively high extraction efficiencies were obtained at higher densities achieved at the low temperature of 40°C (in the vicinity of the critical temperature of CO_2, 31°C) and pressures ranging from 11.0 MPa to 24.1 MPa. The observations made in the current research showed that the highest SC CO_2 density of 0.87 g/mL obtained at 24.1 MPa and 40°C yielded the best extraction efficiency of PHCs from both FP 1 and FP 2. These results suggest that extraction temperatures in the vicinity of the pure solvent's critical temperature may result in higher oil yields with an increase in density, thereby suggesting further that the results obtained in this work are solvent density dependent. It has also been suggested in the literature that SC CO_2 extraction of complex hydrocarbon mixtures such as crude oil is governed by the density of SC CO_2 at those extraction conditions (Hwang et al. 1995). ANOVA performed at a significance level of (p) $\leq 5\%$ on extraction efficiencies obtained at SC CO_2 densities ranging from 0.43 g/mL to 0.87 g/mL showed that there is a significant increase in extraction efficiency with an increase in SC CO_2 density (see Appendix F3). This analysis further emphasized that the SFE process is a solvent density dependent process.

To determine the efficacy of extractions, in the affinity of supercritical conditions for carbon dioxide, whose critical conditions are 31°C and 7.4 MPa, the extraction conditions of 15.2 MPa and 25°C were investigated. Being below the critical temperature of 31°C, this was considered a sub-critical condition. At this condition, the carbon dioxide did not behave as a supercritical fluid but rather as a pressurized liquid with a high density and a high solvating power. It was expected that the liquid like density might increase the extraction efficiency of the process, but the extraction efficiency (Table 4.11) suggested that, although the density at 15.2 MPa and 25°C, and 24.1 MPa and 40°C are similar (0.88g/mL and 0.87g/mL respectively), there is a large difference in the extraction efficiencies obtained at these conditions. The extraction condition of 24.1 MPa at 40°C (0.87%) yielded 89% extraction while 15.2 MPa at 25°C (0.88 g/mL) yielded 61%

extraction. This result suggests that the liquid like density is not the only factor affecting the extraction efficiency and that supercritical conditions are necessary for adequate extraction.

4.2.4.5 Effect of CO_2 flowrate

As seen in Tables 4.7 to 4.12, most of the SC CO_2 extractions were performed at a CO_2 flowrate of 10 mL/min. Only a few extractions were performed at different flowrates to determine the effect of flow rate on the extraction efficiency. For FP 1, SC CO_2 extractions were performed at extraction conditions of 15.2 MPa, 40°C, and at CO_2 flowrates of 1 mL/min, 5 mL/min, and 20 mL/min. Based on the literature available on the influence of flow rate on SC CO_2 extraction, the extraction can be controlled either by a kinetic/desorption step or by a solubility/elution step (Bjorklund et al. 2000).

In this work, extractions were carried out at different flowrates; however, the dynamic extraction time was adjusted to ensure that an equal mass (at least 600 g) of CO_2 flowed through the vessel. Figure 4.23 shows the cumulative mass of PHCs collected with respect to cumulative mass of CO_2 at different flowrates ranging from 1 mL/min to 20 mL/min at extraction conditions of 15.2 MPa and 40°C. This figure only presents data up to a cumulative mass of 600 g of CO_2.

Table 4.10 shows the extraction efficiencies at 15.2 MPa and 40°C at various flowrates of 1 mL/min, 5 mL/min, 10 mL/min and 20 mL/min. The extraction efficiencies of these runs ranged from 71% to 78%, with PHC content ranging from 6980 mg/kg to 9330 mg/kg. ANOVA analyses (see Appendix F3) on the PHC contents obtained at different flowrates at the same extraction conditions suggest that the mean PHC contents for the three groups of flowrates are not significantly different.

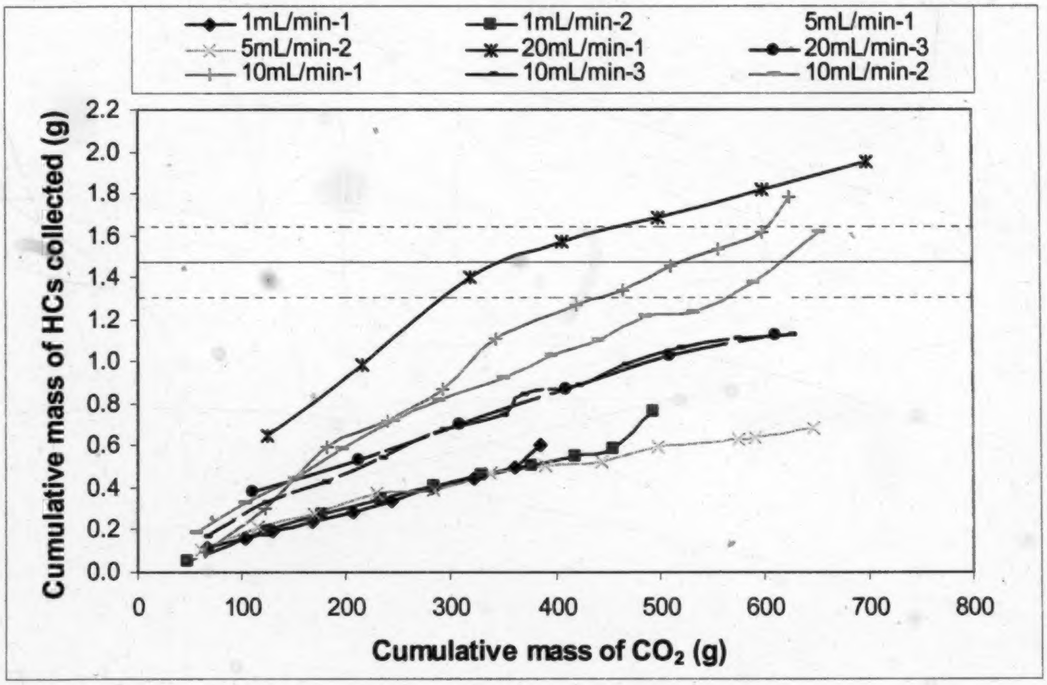


Figure 4.23: Behavior of mass of PHCs collected during SC CO_2 extractions at 15.2 MPa and 40°C at different SC CO_2 flowrates (FP 1)

This result suggests that the different CO_2 flowrates do not affect the extraction efficiency of PHCs extracted from FP 1 provided a similar amount of CO_2 is allowed to flow through the contaminated soil in the extraction vessel during each run (see Appendix F3). It would therefore appear that the extractions and extraction efficiencies are limited by the amount of PHC that can dissolve into a certain mass of CO_2, i.e. the solubility of the PHCs in SC CO_2. As mentioned earlier, all of the experiments investigating flowrate were conducted not based on a fixed time of extraction but based on the mass of CO_2 passing through the contaminated soil. During the experiments, it was observed that the final mass of HCs collected during each extraction run (at different flowrates as seen in Figure 4.23) is different; however, the GC analyses of PHCs extracted showed similar extraction efficiency ranging from 71-78%. These results seem to indicate that, at higher flow rates, compounds other than PHCs or compounds not detected by the GC may have been extracted.

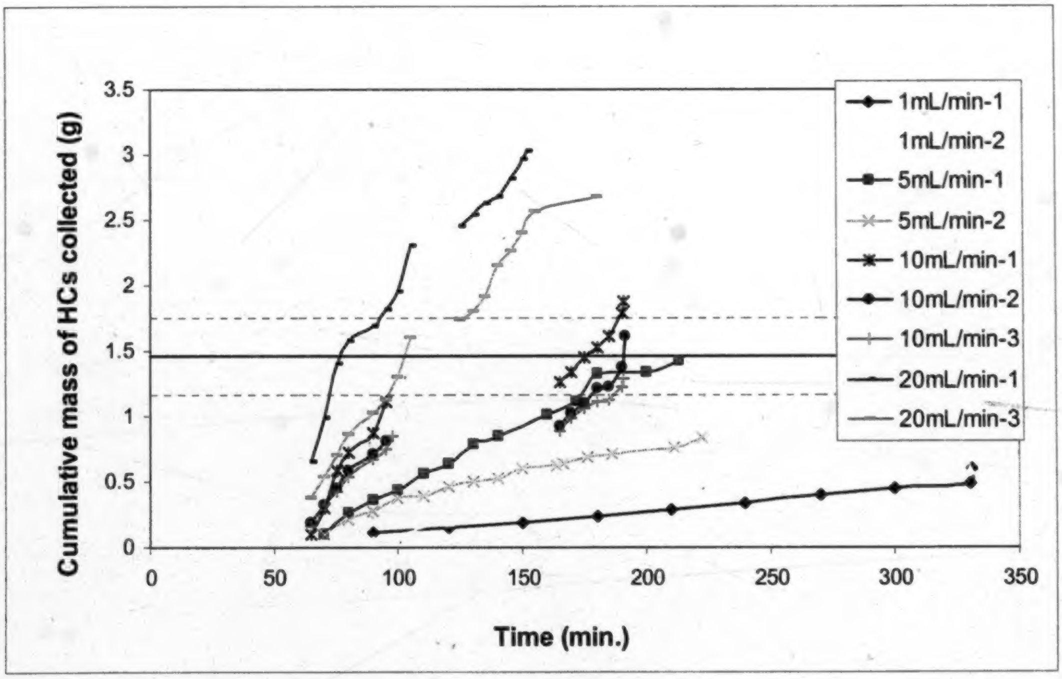


Figure 4.24: Behavior of cumulative mass of PHCs collected irrespective of amount of CO_2 flowing through the vessel (15.2 MPa. 40°C) at different flowrates (FP 1)

On the other hand, Figure 4.24 shows the cumulative mass of HCs collected during dynamic extraction against total extraction time irrespective of the amount of CO_2

flowing through the vessel. Figure 4.24 suggests that the rate of extraction of PHCs increases with an increase in CO_2 flowrate suggesting that the process might be solubility limited. This observation indicates that, if the extractions are run for a specific period of time irrespective of the amount of CO_2 flowing through the vessel, a 20 mL/min CO_2 flowrate will extract higher amount of PHCs.

4.2.4.6 Effect of soil type

The soil properties that affect the SFE process include the type of soil matrix and its physical and chemical properties such as porosity, pore size, particle size distribution and water content (Tomasko et al. 1995). Organic contaminants may be difficult to remove from soils rich in organic material due to the strong bond formation between the organic pollutants and the organic matter present in the soil. The binding and removal of PHCs from the soil is largely influenced by the textural property of the soil and by the amount of organic content and moisture present in the soil (Low and Duffy 1995). The degree of differences in the solubilities and sorption of PHCs in the SCF and on the soil particles, respectively, the moisture content, and the presence of other organic constituents in the soil represent major extraction problems (Morselli et al. 1999; Hawari et al. 1995). The heterogeneous nature of the soil affects the affinity of the contaminant to the soil matrix (Eckert-Tilotta et al. 1993).

The results obtained in the current work are consistent with the observations made in the literature (Cocero et al. 2000; Bowadt and Hawthorne 1995; Tomasko et al. 1995; Eckert-Tilotta et al. 1993; Cai 1990) for the extractions of PHCs from two different soil types (sand and loam). It was found in this study that fine textured loam (FP 2) yielded lower extraction efficiencies as compared to sandy soil (FP 1) at the same extraction conditions (Figure 4.19). For example, total PHC extraction efficiencies of 89% and 80% were obtained at the extraction conditions of 24.1 MPa and 40°C from FP 1 and FP 2, respectively. It is suggested that the smaller the particle size, the larger is the surface area, and therefore the stronger is the affinity of the soil for the contaminant. This increased affinity results in a reduced amount of contaminant available for dissolution into the SCF and thus in a reduced extraction efficiency of the contaminant (Bowadt and Hawthorne 1995; Tomasko et al. 1995; Eckert-Tilotta et al. 1993). Thus, FP 2 (loam) being fine-textured soil has smaller particle size (see Table 3.1), and hence yields lower extraction efficiencies than the coarse-grained FP 1 (sand). Cocero *et al.* (2000) in their study on extraction of the petroleum hydrocarbons from soil also concluded that better extraction efficiencies were obtained from larger particle sized soil. Also, it is believed that of the soil types, clay has the strongest affinity for the organic contaminants followed by loam and silt (Eckert-Tilotta et al. 1993). In addition, this soil being aged and weathered, PHCs might be more strongly adsorbed on to the soil again resulting in less PHCs available for dissolution into the SC CO_2. Cocero et al. (2000) suggested that in the case of aged soils, the effect of interactions between the contaminant and the soil are more important than the effect of particle size. However, due to the unavailable information on the age of the FP 2 in the current study, it is hard to suggest if the effect of aging predominates the effect of particle size.

4.2.5 Chromatograms of PHCs

4.2.5.1 Untreated and treated flare pit soils

Figure 4.25 shows the chromatograms of PHCs obtained from raw untreated FP 1 (as labelled) and treated flare pit soil at 40°C and at 15.2 MPa (top chromatogram) and 24.1 MPa (bottom chromatogram). Similarly, Figure 4.26 shows the raw untreated and treated FP 2 at 15.2 MPa and 40°C. The idea behind showing two chromatograms (top and bottom) in Figure 4.25 is to provide an indication of the efficiency of SC CO_2 extraction in reducing the PHC content from untreated FP 1. Ideally, the baseline for the raw flare pit soil in the bottom chromatogram should descend back to the baseline of the 24.1 MPa treated soil as it does in the top chromatogram, but the GC calibration methods were different in each case. Untreated flare pit soil samples were analyzed using GC Method 1 and flare pit soil treated at 24.1 MPa and 40°C was analyzed using GC Method 2 (see Section 3.2.3.2 for method descriptions).

The chromatograms of the treated FP 1 at 24.1 MPa (Figure 4.25), shows no hump of PHCs until a retention time of 16 minutes, which is close to the retention time window of nC_{34} (Table 4.1). This result shows that the PHC fractions F2 (nC_{10}-nC_{16}) and the F4 fraction (nC_{34}- nC_{50})), this PHC level meet the regulatory criteria as mentioned in Section 4.2.4.3 and as observed from results in Table 4.10. Chromatograms for FP 2 (Figure 4.26) also reflect the data as shown in Table 4.12 and Figure 4.19.

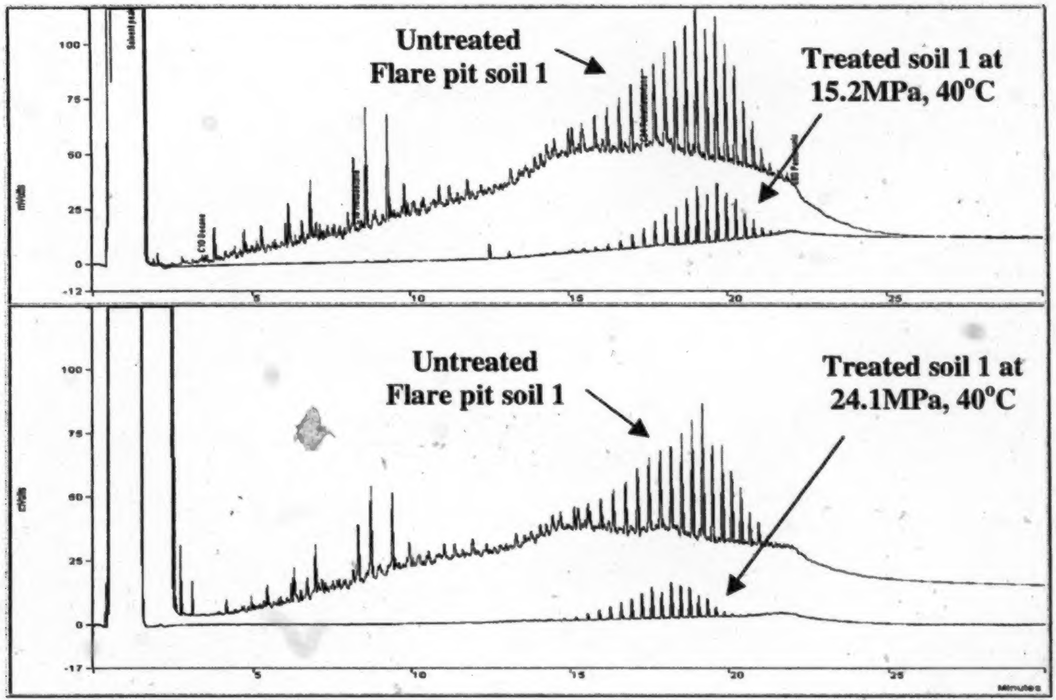


Figure 4.25: Chromatograms of untreated and treated FP 1

No hump of PHCs is observed (for FP 1) until 8 to 9 minutes indicating the high removal of the F2 fraction (98-99% removal) as shown in Figure 4.25. Figure 4.26 shows that the hump for the treated FP 2 starts to decrease slightly from 10 minutes to 17-18 minutes, which represents the F3 fraction of PHCs (nC_{16}-nC_{34}), and then lines up closely with the chromatogram of untreated soil from 17-18 minutes to >20 minutes. This trend of the hump of the treated soil indicates that at 14.8 MPa and 40°C, the F2 fraction has been removed efficiently (98%), the F3 fraction has been removed to some extent (83%) but not to below the regulatory guidelines, and the F4 fraction has been only slightly extracted (25%).

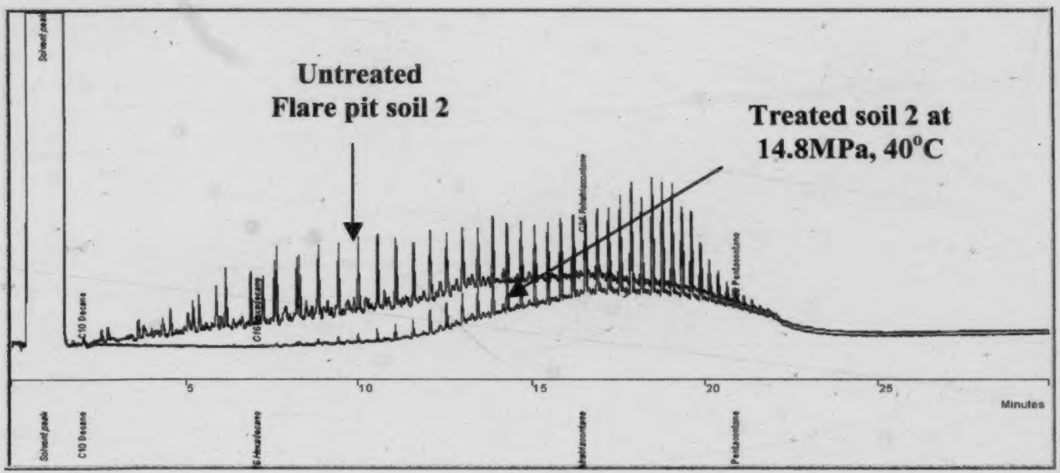


Figure 4.26: Chromatograms of untreated and treated FP 2

4.2.5.2 PHCs trapped in glass vials during SC CO_2 extractions

As mentioned earlier in Section 3.21, during a 30-minute dynamic extraction period, PHCs are collected every 5 minutes, thereby making 12-glass vial traps (for two dynamic extractions) and one solvent trap. The solvent trap was filled with 20 mL of toluene to ensure that no PHCs are lost along with CO_2 flow that is vented into the fumehood. Figure 4.27 shows chromatogram of the PHCs collected in Trap 1 (65 minutes), Trap 12 (180 minutes) and the solvent trap, at 12.4 MPa and 40°C for FP 1. Figure 4.28 provides chromatograms obtained from PHCs extracted at 15.2 MPa and 80°C and shows chromatograms of Trap 1 (65 min), Trap 6 (90 min) and Trap 12 (180 min) for FP 1. These chromatograms indicate that different PHC fractions are extracted during different stages of the dynamic extraction. The difference in the heights of the chromatograms is mainly due to the difference in the concentrations of the injected GC sample than that of the extracted oil from the soil samples.

Figure 4.27 shows that the PHCs in Trap 1 mainly consist of F2 and some F3 fraction of PHCs, while those in Trap 12 consist of mostly F3 and some F4 fraction of PHCs. The chromatogram of the PHCs collected in the solvent trap confirmed that there are lighter HCs that tend to flow out along with the CO_2, some or all of which can be trapped by the solvent trap. The chromatogram suggests that the lighter HCs trapped in the solvent trap may include some PHCs abut also other contaminants or other lighter end compounds (other than PHCs) that were extracted from the soil during SFE.

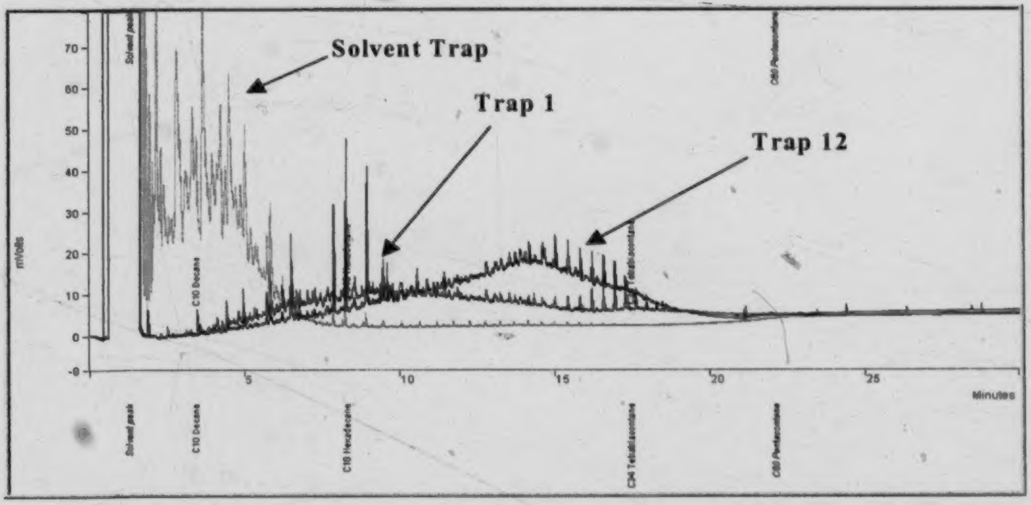


Figure 4.27: Chromatograms of Trap 1 (65 min), Trap 12 (180 min) and solvent Trap at 12.4MPa and 40°C for FP 1

The temperature of the extraction run being 40°C, the lighter hydrocarbons including some of F2 and F3 fractions may be volatilized easily and are therefore collected during the early stages of dynamic extraction (Trap 1). On the other hand, heavier PHCs basically (F3 and some F4 fraction) might have been strongly bound to the soil but the 60-minute static extraction time allowed during the SC CO_2 extraction before starting second dynamic extraction, might have helped in the desorption of heavier PHCs from the soil into the SC CO_2. As mentioned previously, more experiments with less static extraction time needs to be performed.

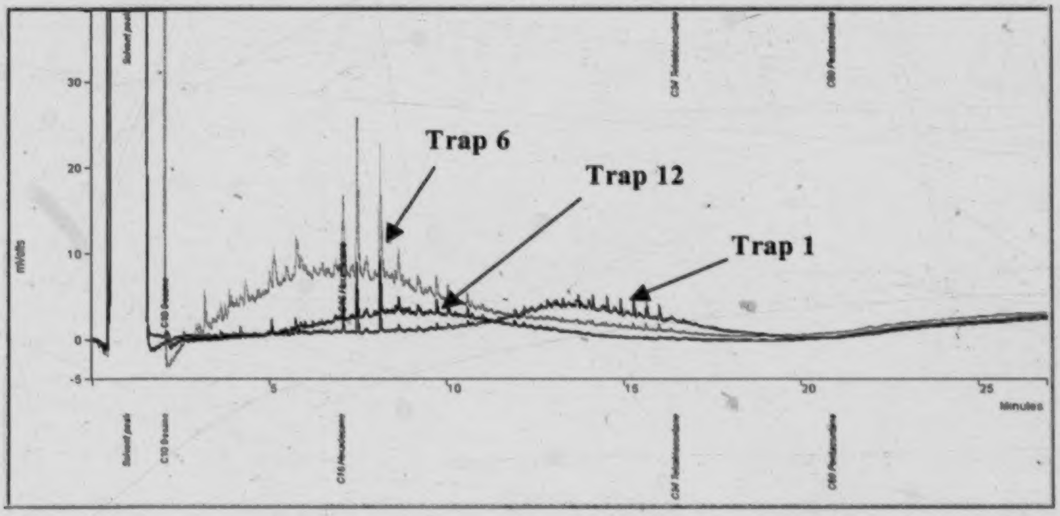


Figure 4.28: Chromatograms of Trap 1 (65 min), Trap 6 (90 min) and Trap 12 (180 min) at 15.2 MPa and 80°C for FP 1

The observation that earlier extracts collected during the dynamic extraction contain lighter compounds and later extracts contain heavier HCs is consistent with observation made by Hwang et al. (1995) in their study. Hwang et al. (1995) suggested that greater amount of naphthenic and aromatic compounds were extracted at earlier extraction times as compared to paraffinic compounds. Morselli et al. (1999) also found that mid-range HCs ranging from C_{18}-C_{35} were most strongly retained by the soil, and higher HCs ($>C_{35}$) have higher force of sorption.

Figure 4.28 provides chromatograms obtained from PHCs extracted at 15.2 MPa and 80°C suggest that higher temperatures might have increased the volatilization of HCs, mainly heavier HCs (F3 and F4 fraction), which usually otherwise require either time or high temperature to be extracted. As a result, the PHCs collected during the early stages of 1st dynamic extraction are heavier (Figure 4.28) ranging from $>nC_{16}$ to $>nC_{34}$. The other two traps, Trap 6 collected at 90 minutes and Trap 12 collected at 180 minutes indicate that the F2 and F3 fractions of PHCs are extracted throughout the remainder of the extraction.

Another set of chromatograms obtained for the traps collected at lowest CO_2 flow rate of 1 mL/min at SC CO_2 extraction conditions of 15.2 MPa and 40°C for FP 1 is shown in Figure 4.29. These chromatograms suggest that at low flowrates, similar fractions of PHCs (F2 and F3 fraction) were extracted throughout the entire extraction. A chromatogram of the bypass trap that was conducted at the end of the extraction run to clean the lines downstream of the vessel with SC CO_2, suggests that heavier PHCs (mainly F3 and F4) were trapped in the lines accounting for about 0.2g of PHCs out of a total of 0.7 g extracted PHCs.

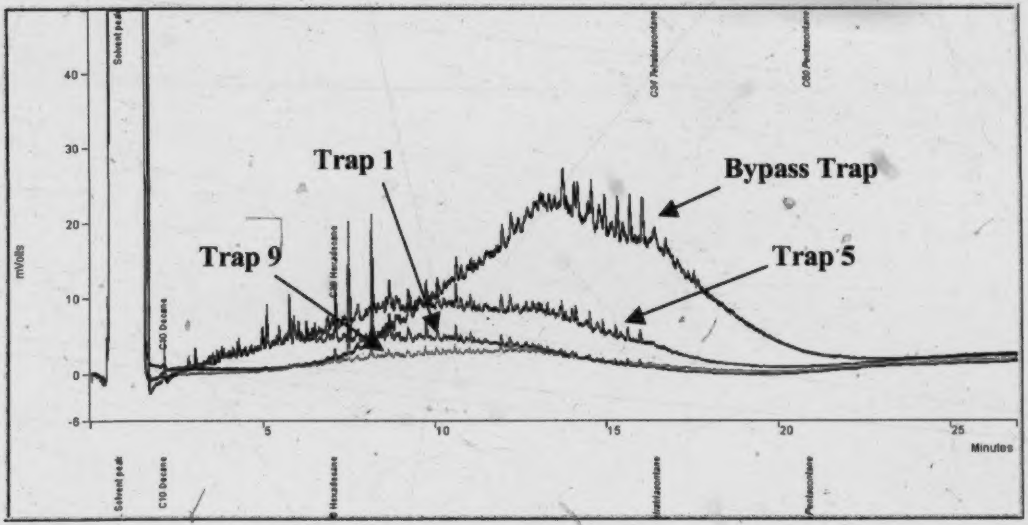


Figure 4.29: **Chromatograms of Trap 1 (30 min), Trap 5 (210 min), Trap 9 (330 min) and bypass trap at 15.2 MPa for FP 1**

4.26 Mass of PHCs collected

Figures 4.30 and 4.31 show the plot of the mass of PHCs collected during the SC CO_2 extraction performed at 24.1 MPa and 40°C for FP 1, and for FP 2. Each double cycle SC CO_2 extraction performed consists of two 60-minute static extraction periods (denoted as S1 and S2 in the figures below), each followed by a 30-minute dynamic extraction period (denoted as D1 and D2 in Figures 4.30 and 4.31) during which PHCs are collected every 5 minutes. The trend of collection of PHCs is shown in Figures 4.30 and 4.31. Data for this plot are provided in Table G-1 in Appendix G. Both Figures 4.30 and 4.31 indicate that the mass of PHCs extracted does not follow a distinct trend.

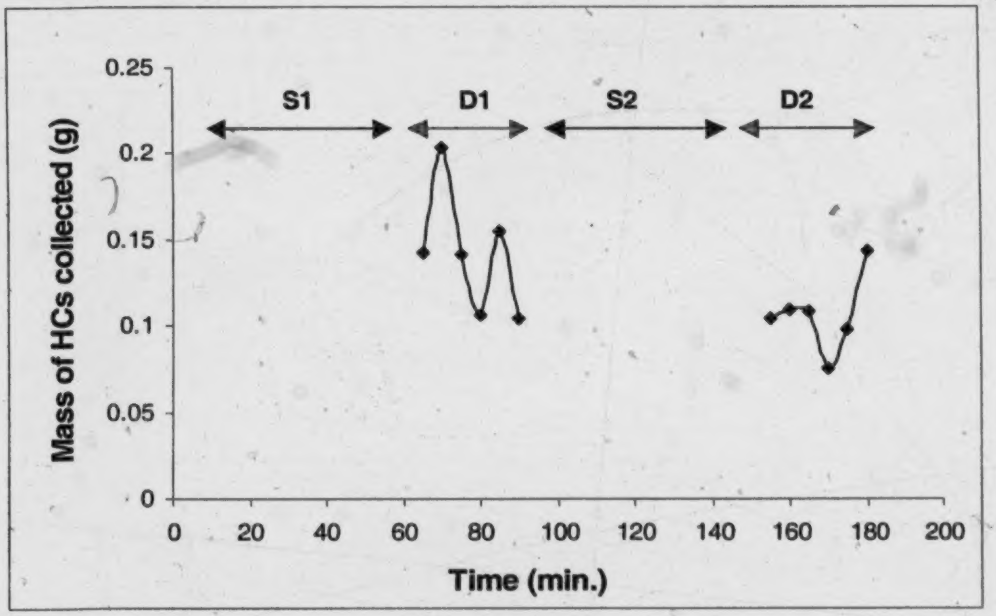


Figure 4.30: Mass of HCs collected with time during SC CO_2 extraction at 24.1MPa for FP 1

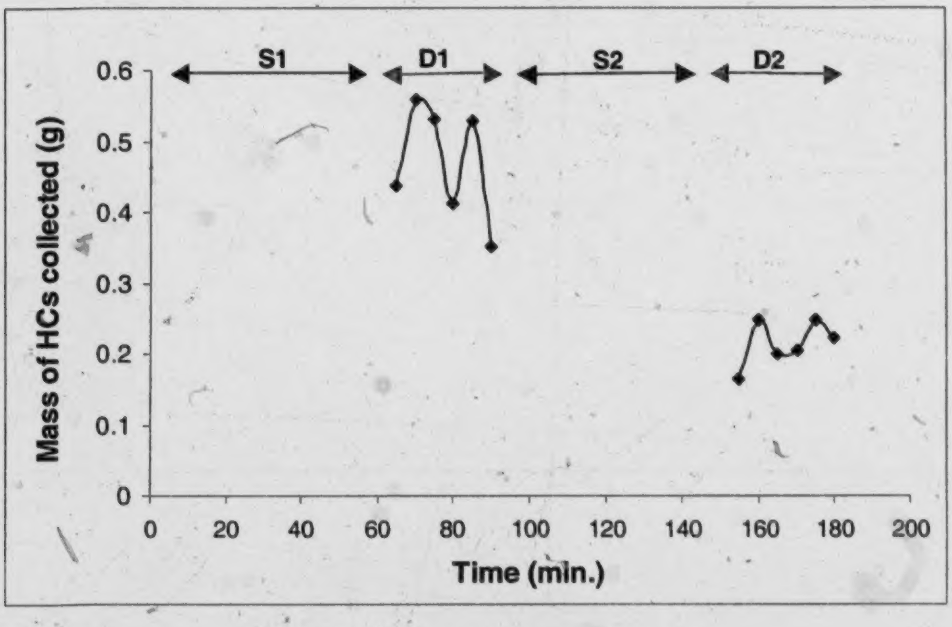


Figure 4.31: Mass of HCs collected with time during SC CO_2 extraction at 24.1 MPa for FP 2

Similar amounts of PHCs were extracted after the second static extraction of one hour in Figure 4.30, whereas a lower amount of HCs were collected from FP 2 under the same conditions (Figure 4.31). Considering all the SC CO_2 extraction conditions, some of the extraction conditions showed higher extraction after second static extraction, some showed lower or almost similar extraction of PHCs after a second static extraction period of 1 hour. Due to these different observations, it cannot be concluded that a static extraction period of one hour that was usually practised for all SC CO_2 extraction conditions is effective. More experiments with less time for second static extraction and with no second static extraction (single extractions) should be performed in order to reach a definite conclusion.

4.3 VARIABILITY IN RESULTS

Tables 4.7 and 4.8 provide the PHC results obtained for untreated and treated FP 1 at various extraction conditions, with pressures ranging from 11.0 MPa to 24.1 MPa and temperatures ranging from 25°C to 80°C. Both tables show that the relative standard deviations (i.e. ratio of standard deviation to mean, expressed in percentage) ranged from 10% to 76%. The high standard deviations may be attributed primarily to the heterogeneity of the soil sample, uncontrollable variables during the experiments and to the variability in GC analyses. The soil being investigated was 54 year old, highly weathered, PHC contaminated soil. Proper or ideal homogenization of this soil seemed impossible due to the presence of sticky, agglomerated particles of soil; however, efforts were made to sieve the soil down to 2mm particle size (see Section 3.1.1). Other uncontrollable variables during SFE extractions were the variability in CO_2 flow rate, variability in the extracted soil's sub-sampling, possible incomplete Soxhlet extraction, and variability in the GC analyses. A visual observation of the color difference of the two SFE treated FP 1 soil samples (layered on top of each other for comparison purposes), treated at the same extraction conditions of 20.7 MPa and 40°C (see Figure 4.32) adds to the explanation of the high relative standard deviations ranging from 10% to 76%. The observations in Figure 4.32 may support the importance of soil heterogeneity and uncontrollable variables in the SFE extraction as being important factors in explaining the high standard deviations.

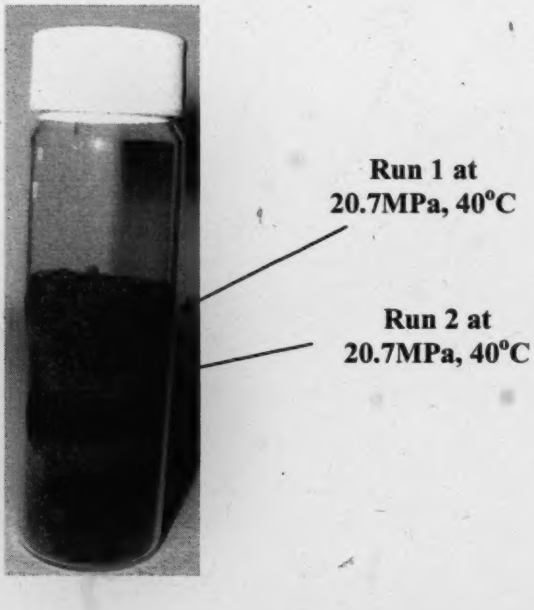


Figure 4.32: Two SFE treated FP 1 soil samples obtained from Run 1 and Run 2 performed at 20.7 MPa and 40°C (layered on top of each other)

Similarly, Table 4.9 shows the results for PHC analyses obtained for raw and treated FP 2 at various extraction conditions ranging from 13.8 MPa to 24.1 MPa and 40°C. Due to time limitations, only the extraction conditions that were considered optimal for FP 1 were used to perform extractions on FP 2. Table 4.9 shows that the relative standard deviations for FP 2 ranged from 6% to 54%. Again, the high standard deviations may be due to the heterogeneity of the soil sample, variability in sampling, and uncontrollable operational variables during SFE extractions, Soxhlet extractions, and GC analyses.

To investigate the variability in results, two double cycle extraction runs performed at 15.2 MPa and 40°C for FP 1, and at 14.8 MPa and 40°C for FP 2 are presented in Table 4.13 and Table 4.14. These tables show the variability in results obtained for FP 1 and FP 2 due to GC injections, sub-sampling and SFE extractions. As mentioned earlier, for a particular extraction condition, three sub-samples of each of the duplicate SFE extractions were prepared for GC/FID analyses. Triplicate GC injections of each of the three sub-samples were carried out for all extraction conditions. Tables 4.13 and 4.14 show the relative standard deviations obtained for the triplicate injections for each of the three sub-samples, and for the average of the triplicate injections for each of the three sub-samples.

The SC CO_2 double cycle extraction conditions shown in Table 4.13 and Table 4.14 were chosen based on the highest relative standard deviations (RSDs) for the respective soils at those conditions. Tables 4.7 to Table 4.9 show that in this work, % RSDs for the mean PHC content for the SC CO_2 extractions of FP 1 and FP 2 at various extraction conditions ranged from 6% to 76%. Table 4.13 and Table 4.14 are provided as examples of the variability in the results obtained within triplicate GC injections from one sub-sample to another for an extraction run, and all GC injection results from one extraction batch to another extraction batch at the same extraction conditions. The relative standard deviations for the triplicate GC injections for each of the sub-samples obtained at same extraction conditions ranged from 49% to 109% as provided in Table 4.13.

Table 4.13: Results of PHC extraction from FP 1 using SC CO_2 double cycle extractions at 15.2 MPa and 40°C (SC CO_2 flow rate of 1 mL/min)

Run	Sub-sample	GC Injections	PHCs (mg/kg)	Total PHCs content (%)					
				Triplicate GC Injections			SC CO_2 extraction batch		
				Mean (mg/kg)	SD	RSD (%)	Mean	SD	RSD (%)
1	1	1	17334	9131	7114	78	**7180**	5500	**76**
		2	4643						
		3	5417						
	2	1	2136	6570	7161	109			
		2	2742						
		3	14831						
	3	1	4741	5840	2864	49			
		2	3689						
		3	9091						
2	1	1	4919	6959	3696	53	**7577**	3600	**48**
		2	11225						
		3	4732						
	2	1	4928	8043	4496	56			
		2	6003						
		3	13197						
	3	1	5219	7729	4240	55			
		2	12624						
		3	5344						

Table 4.14: Results of PHC extraction from FP 2 using SC CO_2 double cycle extraction at 14.8 MPa and 40°C (SC CO_2 flow rate of 10 mL/min)

Run	Sub-sample	GC Injections	PHCs (mg/kg)	Total PHCs content (%)					
				Triplicate GC Injections			SC CO_2 extraction batch		
				Mean (mg/kg)	SD	RSD (%)	Mean	SD	RSD (%)
1	1	1	24588	25062	17916	71	**34196**	17400	**51**
		2	7387						
		3	43210						
	2	1	8533	30692	21676	71			
		2	31693						
		3	51850						
	3	1	41838	46836	6419	14			
		2	44594						
		3	54075						
2	1	1	46606	47414	797	2	**37345**	20000	**54**
		2	47438						
		3	48199						
	2	1	16088	17132	2498	15			
		2	15326						
		3	19983						
	3	1	52271	47487	25963	55			
		2	70725						
		3	19465						

The high RSDs of 78% and 109% for FP 1 were the result of the high value of PHC content determined from the first GC injection of the first sub-sample obtained from Run 1, and from the third GC injection of the second sub-sample of Run 1 as presented in Table 4.13. Similarly, Table 4.14 for FP 2 shows that the relative standard deviations for the triplicate GC injections for each of the sub-samples obtained under similar extraction conditions ranged from 2% to 71%.

The 71% RSD for the first and the second sub-samples obtained from Run 1 were the result of the low PHC content determination from the second GC injection of the first sub-sample, and the first GC injection of the second sub-sample of Run 1. Also, the % RSDs for the two SC CO_2 extraction runs (based on an average of 9 GC injections for each extraction run) performed at the same extraction conditions were found to be 76% and 48% for Run 1 and Run 2, respectively, for FP 1, and 51% and 54% for Run 1 and Run 2 respectively, for FP 2 (see Tables 4.13 and 4.14).

In order to identify which factors (for example SFE extraction runs, sub-samples, or GC analyses) accounted for the increase in the variability of the results, analysis of variance (ANOVA) calculations were performed at significance level of (p) ≤5%.. ANOVA analysis of the data shown in Tables 4.13 and Table 4.14 are presented in Appendix F4. ANOVA analyses for the difference in the mean PHC content for the three FP 1 sub-samples (see Table 4.8) obtained from the double cycle extractions performed on 04 July, 2003 (Run 1) and 14 July, 2003 (Run 2) suggest that there is no difference in the mean HC content for the sub-samples analyzed. This result suggests that the mean PHC contents of each sub-sample batch obtained during each of the two extraction runs performed at same extraction conditions are similar. On the other hand, ANOVA analyses of the sub-samples analyzed for the SC CO_2 extractions performed on 20 March, 2003 (Run 1) and 01 July, 2003 (Run 2) for FP 2 suggest that while no difference in the mean PHC content was observed for the sub-samples analyzed for the extraction performed on 20 March, 2003, a difference in the mean PHC content for the sub-samples analyzed on 01 July, 2003 was observed. These ANOVA analyses suggest that the PHC content determination may or may not be different from one sub-sample batch to another for the same extraction conditions. It might be dependent on each SC CO_2 extraction performed. To confirm this, ANOVA analysis was performed at 95% confidence interval on the two groups of PHC contents obtained during SC CO_2 extraction Run 1 and Run 2 performed for both the soils (see Appendix F5). The analyses suggested that for both FP 1 and FP 2, no significant difference between the mean PHC contents of Run 1 and Run 2 were observed. This observation implied that the two extraction runs performed at the same extraction conditions, in spite of their high relative standard deviations can be considered duplicates of each other. In other words, Run 1 and Run 2 give similar results at the same extraction conditions.

Raw flare pit soil samples of both soil 1 and soil 2 were sent to external laboratories and analyzed in-house. The results of in-house analysis and of external laboratory analyses are provided in Table 4.15. The results of PHCs obtained from both in-house and external analyses for FP 1 are quite similar. While in case of FP 2, however, the results of in-house analyses show lower values than the ones obtained from of external analyses. No samples for SC CO_2 extracted soils were sent for analyses to commercial lab due to cost considerations, the fact that analysis turnaround time and quality control were beyond the scope of this work.

As mentioned earlier in Section 4.2.4.1 that the extraction efficiency values for both FP 1 and FP 2 were calculated using PHC content values that were averages of in-house analyses and commercial lab analyses. For FP 1, the extraction efficiencies were calculated using a PHC content value of 31700 mg/kg, which is an average of values obtained from in-house analysis (31200 mg/kg) and commercial lab (32300 mg/kg). For FP 2, the extraction efficiencies were calculated using a PHC content value of 112600 mg/kg, which is an average of values obtained from in-house analysis (105200 mg/kg), and two external analyses (115000 mg/kg and 117000 mg/kg).

Table 4.15: Raw flare pit soil analyses results obtained in-house and other laboratory

Soil	*In House*	*External laboratories*
Raw FP 1	3.12% (n=5, SD=0.77%)	Lab 1: 3.23% (n=4, SD=0.38)
Raw FP 2	10.52% (n=4, SD= 2.4%)	Lab 1: 11.55%, (n=2) Lab 2: 11.77% (n-=1)

It was observed however that for both FP 1 and FP 2, the total extraction efficiencies of PHCs were not substantially affected if only in-house analyses values were used. However, it does affect the extraction efficiency of the individual PHC fractions (F2, F3, F4), in particular, the F4 fraction. For example, total extraction efficiencies of 89% and 79% were observed for FP 1 and FP 2, respectively, at 24.1 MPa and 40°C, using the PHC values obtained from in-house analysis (31200 mg/kg for FP 1 and 105200 mg/kg for FP 2). These values of extraction efficiencies are quite similar to the ones obtained by using PHC value that was an average of values obtained from both in-house and external labs (89% for FP 1 and 80% for FP 2), see Table 4.10 and 4.12. Calculations based solely on the in-house analyses values obtained for FP 1 and FP 2 showed that the extraction efficiencies for PHC fractions F2, F3, and F4 obtained at 24.1 MPa and 40°C were 98%, 98% and 68%, respectively for FP 1 and 99%, 95% and 31%, respectively for FP 2. Again, these extraction efficiencies for each of the fractions are quite similar to those obtained if the average was used (see Table 4.10 and 4.12), except for the lower values that are obtained for F4 fraction.

These results therefore indicate that using the average value from in-house and external lab analyses versus using only in-house analyses for calculating the PHC content of the untreated flare pit soils does not substantially affect the values of the calculated extraction efficiencies. In addition, the conclusions drawn from these calculated extraction efficiencies do not change if averages of the different data or solely in-house data were used.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Described below are the conclusions that were drawn from the results obtained in this work.

SC CO_2 Extraction results

Double cycle SC CO_2 extractions have been able to successfully extract PHCs ranging from nC_{10}-nC_{50} from flare pit soils. GC analyses of the PHC content of the SFE treated flare pit soil samples indicate that appreciable amounts of PHCs were extracted from the two-studied soil samples. Extraction efficiencies ranging from 44% to 89% for the sandy flare pit soil 1 (FP 1) and from 58% to 80% for fine loam (flare pit soil 2, FP 2) were obtained at the conditions tested in this work. It was also noted that a decrease in the extraction efficiency of PHCs was obtained with an increase in temperature at a constant pressure condition. A greater effect on the extraction efficiency of PHCs was observed at a lower temperature of 40°C, when the density of SC CO_2 increased with an increase in pressure from 11.0 MPa to 24.1 MPa. The SC CO_2 extracted soils appeared to be drier, grainy and lighter in appearance. For FP 1, which is sandy in texture, F2 (nC_{10}-nC_{16}) and F3 (nC_{16}-nC_{34}) fractions can be extracted below CCME levels required for soil quality criteria (CCME 2001-a) by treating flare pit soil above 13.4 MPa and 40°C, while the F4 (nC_{34}-nC_{50}) fraction can meet the regulatory criteria when treated at or above 24.1 MPa and 40°C. F2 (nC_{10}-nC_{16}) for FP 2, which was a fine textured loam, the F2 fraction was extracted and brought below CCME soil quality levels at or above SC CO_2 extraction conditions of 14.8 MPa and 40°C. The F3 fraction of FP 2 met CCME soil criteria at 24.1 MPa and 40°C. More extraction conditions need specifically higher pressures to be investigated to achieve better extraction of the F4 fraction of PHCs from flare pit soils.

The difference in the ease of extraction of F3 and F4 fraction from the two soils confirms that extraction of contaminant from the soils highly depends on the nature and type of the soil. It was difficult to extract heavier PHCs from fine-textured loam as compared to coarse grained-sandy flare pit soil thus showing that the type of soil matrix and its physical and chemical properties affect the efficiency of the SFE process.

Statistical analysis of the results obtained at different SC CO_2 flowrates suggested that different SC CO_2 flowrates used during dynamic extraction following a static extraction period do not affect the extraction efficiency of PHCs extracted from flare pit soils provided similar amounts of CO_2 are allowed to flow through the contaminated soil in the extraction vessel during each run.

Optimum extraction conditions for treatment of FP 1 were found to at or above 24.1 MPa and 40°C. Although consistently higher extraction efficiencies ranging from 83 to 89% were obtained for total PHCs extraction for FP 1 at or above 13.8 MPa and 40°C, higher pressures were needed to better remove the F4 (C_{34}-C_{50}) fraction of PHCs below regulatory levels. Conditions of 24.1 MPa and 40°C were considered optimal. At this optimal condition, extraction efficiencies of 100%, 98% and 73% were obtained for the F2, F3 and F4 fractions of PHCs respectively, thus achieving the regulatory limit as required by the CCME. However, for FP 2, no optimal extraction conditions for the extraction of all the three PHC fractions (F2, F3 and F4) were found that could bring the soil quality as required by CCME (2001b). Only F2 and F3 fraction levels were found to meet CCME soil quality criteria at or above extraction conditions of 24.1 MPa and 40°C. Although, the results show a high relative standard deviation of up to 76%, these deviations might have resulted in part from inherent drifts experienced in chromatographic analyses, and potentially due to the highly heterogeneous nature of the old and weathered real flare pit soils.

Chromatograms of the PHCs collected every five minutes during each of the two-30 minute dynamic extraction period suggest that lighter end (F2 fraction) of the HCs are extracted during the early stages of the dynamic extraction, while heavier HCs (F3 and F4) are extracted during the later stages. This result indicates that time is an important factor in the extraction of PHCs.

PHCs collected in the vials showed a difference in the colour of the HCs colleted during dynamic extractions. Extraction conditions with less pressure yielded lighter oil (light yellow), which darkened with increase in extraction pressure (dark yellow/brown).

5.2 RECOMMENDATIONS

Supercritical fluid extraction lab-scale Setup

Water needs to be replaced with oil so as to serve as the heat exchanger fluid in heating up the vessel by circulating through the insulated jacket surrounding the vessel.

This replacement would assist in the investigation at higher extraction temperatures (>100°C).

SC CO_2 extractions

More experiments should be performed with different time periods for 1st and 2nd Static extraction period. This would help in finding how effective is the static extraction period of 1 hour in extraction of PHCs from contaminated flare pit soils.

5.3 SUGGESTIONS FOR FUTURE WORK

Water content effect

In this work, the extraction efficiencies of PHCs extracted from flare pit soils were bracketed between 0% and 9% moisture removal assumption. More experiments needs to be conducted with proper moisture content determination before and after extraction so that the exact amount of water extracted during the extraction can be established.

CHAPTER 6 REFERENCES

AEP. (1994). "Alberta Tier I Criteria for Contaminated Soil Assessment and Remediation." Alberta Environmental Protection, Soil Protection Branch, Edmonton, Alberta.

AEP. (2001). "Alberta Soil and Water Quality Guidelines for Hydrocarbon at Upstream Oil and Gas Facilities (Draft)." Edmonton, Alberta.

AEUB. (1996a). "EUB Policy update and Clarification on the use of Earthen Pits." Alberta Energy and Utility Board., Calgary, Alberta.

AEUB. (1996b). "Oilfield Waste Management Requirements for the Upstream Oil and Gas Industry." Alberta Energy and Utilities Board, Calgary, Alberta.

AEUB. (1998). "Suspension, Abandonment, Decontamination, and Surface and Reclamation of Upstream Oil and Gas Facilities." Alberta Energy and Utility Board, Calgary, Alberta.

AEUB. (2001). "Storage Requirements for the Upstream Oil and Gas Industry." Alberta Energy and Utilities Board, Calgary, Alberta.

Akgerman, A. (1993). "Supercritical fluid extraction of contaminants from environmental matrices." *Waste Management*, 13, 403-415.

Amatya, L. P., Hettiaratchi, A. J., and Joshi, C. R. (2002). "Biotreatment of flare pit waste." *Journal of Canadian Petroleum Technology*, 41 (9), 1-7.

Andrews, A. T., Ahlert, A. C., and Kosson, D. S. (1990). "Supercritical fluid extraction of aromatic contaminants from a sandy loam soil." *Environmental Progress*, 9 (4), 204-210.

April, T. M., Foght, J. M., and Currah, R. S. (2000). "Hydrocarbon-degrading filamentous fungi isolated from flare pit soils in northern and western Canada." *Canadian Journal of Microbiology*, 46 (1), 38-49.

AutoclaveEngineers. (2002). "300 cc Bolted closure pressure vessel assembly." Supplied to Civil and Environmental Engineering, University of Alberta, Edmonton, AB by Autoclave Engineers, A division of Snap-tite Inc., Erie, Pennsylvania, U.S.A.

Baheri, H., and Meysami, P. (2002). "Feasibility of fungi bioaugmentation in composting of a flare pit soil." *Journal of Hazardous Materials*, B89, 279-286.

Beaudin, N. R. F., Caron, R. L., Ramsay, J. L., and Ramsay, B. (1996). "Cocomposting of weathered hydrocarbon-contaminated soil." *Compost Science and Utilization*, 4 (2), 35-45.

Bjorklund, E., Bowadt, S., Mathiasson, L., and Hawthorne, S. B. (1999). "Determining PCB sorption/desorption behavior on sediments using selective supercritical fluid extraction. 3. Sorption from water." *Environmental Science & Technology*, 33 (18), 3152-3159.

Bjorklund, E., Nilsson, T., Bowadt, S., Pilorz, K., Mathiasson, L., and Hawthorne, S. B. (2000). "Introducing selective supercritical fluid extraction as a new tool for determining sorption/desorption behavior and bioavailability of persistent organic pollutants in sediment." *Journal of Biochemical and Biophysical Methods*, 43 (1-3), 295-311.

Bowadt, S., and Hawthorne, S. B. (1995). "Supercritical-fluid extraction in environmental analysis." *Journal of Chromatography A*, 703 (1-2), 549-571.

Brady, B. O., Kao C. C, Dooley, K. M., Knopf, F. C., and Gambrell, P. R. (1987). "Supercritical extraction of toxic organics from soils." *Industrial Engineering Research*, 26 (2), 261-268.

Bright, F. V., and McNally, M. P. (1992). *Supercritical fluid technology : theoretical and applied approaches to analytical chemistry*, American Chemical Society., Washington, DC.

Brunner, G. "Processing of natural materials by supercritical gases." *Proceedings of 5th meeting on Supercritical fluids materials and Natural Products Processing. ISASF*, Nice, France.

Burk, R. C., and Kruus, P. (1990). "Supercritical fluid extraction of trace organics from solids." *Journal of Environmental Science and Health*, B25 (5), 553-567.

Cai, J. Y. (1990). "Supercritical fluid extraction of toxic organics from soils," Dissertation.

CAPP. (1996). "Reclamation of pits and ponds." Canadian Association of Petroleum Producers pub #1996-0004.

CAPP. (1997). "The Bio-Reactor project: 1994-95 annual report: the bioremediation of flare pit material." *Publication# 1997-0010*, Canadian Association of Petroleum Producers, Calgary, Alberta.

Caredda, A., Marongiu, B., Porcedda, S., and Soro, C. (2002). "Supercritical carbon dioxide extraction and characterization of *Laurus nobilis* essential oil." *Journal of Agricultural and Food Chemistry*, 50 (6), 1492-1496.

Catalan, J. J. L., Jamaluddin, M. A., Moore, G. R., Ursenbach, G. M., Okazawa, N., and Mehta, A. S. (1998). "Flare pit waste remediation by low temperature oxidation." *Journal of Canadian Petroleum Technology*, 37 (11), 35-43.

CCME. (2001a). "Canada-Wide Standards for Petroleum Hydrocarbons (CWS PHC) in Soil." Winnipeg, Manitoba, http://www.ccme.ca/assets/pdf/phcs_in_soil_standard_e.pdf.

CCME. (2001b). "Canadian Soil Quality Guidelines for the protection of Environmental and Human Health." Winnipeg, Manitoba,.

CCME. (2001c). "Reference Method for Canada-Wide Standard for Petroleum Hydrocarbons in Soil-Tier 1 Method." Winnipeg, Manitoba, http://www.ccme.ca/pdfs/final_phc_method_rvsd_e.pdf.

CCME. (2001-a). "Canadian Soil Quality Guidelines for the protection of Environmental and Human Health." Canadian Council of Ministers of Environment.

CCME. (2001-c). "Reference Method for Canada-Wide Standard for Petroleum Hydrocarbons in Soil-Tier 1 Method." Canadian Council of Ministers of Environment, http://www.ccme.ca/pdfs/final_phc_method_rvsd_e.pdf.

Chaw, D., and Stoklas, U. (2001). "Cocomposting of cattle manure and hydrocarbon contaminated flare pit soils." *Compost Science and Utilization*, 9 (4), 322-335.

Chen, P., Zhou, W., and Tavlarides, L. L. (1997). "Remediation of polychlorinated biphenyls contaminated soils/sediments by supercritical fluid extraction." *Environmental Progress*, 16 (3), 227-236.

Chester, T. L., Pinkston, J. D., and Raynie, D. E. (1998). "Supercritical fluid chromatography and extraction." *Analytical Chemistry*, 70 (12), 301R-319R.

Clifford, T. (1999). *Fundamentals of supercritical fluids*, Oxford University Press., New York.

Cocero, M. J., Alonso, E., and Lucas, S. (2000). "Pilot plant for soil remediation with supercritical CO_2 under quasi-isobaric conditions." *Industrial & Engineering Chemistry Research*, 39 (12), 4597-4602.

Cook, S. V., Chu, A., and Goodman, R. H. (2002). "Leachability and toxicity of hydrocarbons, metals and salt contamination from flare pit soil." *Water Air and Soil Pollution*, 133 (1-4), 297-314.

Danielson, R. M. (1990). "Disposal of oilfield waste by land treatment: summary report on feasibility, environmental risk assessments and future land use." Canadian Association of Petroleum Producers, Calgary, Alberta.

David, F., Verschuere, M., and Sandra, P. (1992). "Offline supercritical fluid extraction capillary GC applications in environmental analysis." *Fresenius Journal of Analalytical Chemistry*, 334 (10-11), 479-485.

Donohue, M. D., Geiger, J. L., Kiamos, A., and Nielsen, K. A. (1996). "Reduction of volatile organic compound emissions during spray painting - A new process using supercritical carbon dioxide to replace traditional paint solvents." *Green chemistry. ACS symposium series*, 626, 152-167.

Dooley, K. M., Ghonasgi, D., Knopf, F. C., and Gambrell, R. P. (1990). "Supercritical CO_2-cosolvent extraction of contaminated soils and sediments." *Environmental Progress*, 9 (4), 197-203.

Dooley, K. M., R., G., and Knopf, F. C. (1987). "The use of entrainers in the Supercritical fluid extraction of soils contaminated with hazardous organics." *Industrial & Engineering Chemistry Research*, 25 (10), 2058-2062.

Eckert-Tilotta, S. E., Hawthorne, S. B., and Miller, D. J. (1993). "Supercritical fluid extraction with carbon dioxide for determination of total petroleum hydrocarbons in soil." *Fuel*, 72, 1015-1023.

Elkanzi, E. M., and Singh, H. (2001). "Extraction of used lubricating oils with supercritical carbon dioxide." *The Arabian Journal for Science and Engineering*, 26 (26C), 11-23.

Eller, F. J., and King, J. W. (2000). "Supercritical carbon dioxide extraction of cedarwood oil: a study of extraction parameters and oil characteristics." *Phytochemical Analysis*, 11 (4), 226-231.

Erkey, C. M., Orejuela M., and Akgerman A. (1993). "Supercritical carbon dioxide extraction of organic from soil." *Environmental Science and Technology*, 27, 1225-1231.

EUB. (1996). "Oilfield Waste Management Requirements for the Upstream Oil and Gas Industry." Alberta Energy and Utilities Board.

EUB. (1996-b). "Oilfield Waste Management Requirements for the Upstream Oil and Gas Industry." Alberta Energy and Utilities Board.

FRTR. (2002). "Remediation technologies screening matrix and reference guide, version 4.0." Federal Remediation Technologies Roundtable.

Gamse, T., and Marr, R. "High pressure extraction of halogenated flame retardents from electronic waste using CO_2 and modifiers." *Sixth Conference on Supercritical Fluids and their Applications*, Maiori, Italy.

Green, J. (1997). "Environmental Impacts of flare pits at Oil and Gas Well sites in Alberta. Eco Research Chair Environmental Risk Management Research Report RR97-1." *RR97-1*, University of Alberta, Edmonton, Alberta.

Hawari, J., Beaulieu, C., Ouellette, D., Pontbriand, Y., Halasz, A. M., and Vantra, H. (1995). "Determination of petroleum-hydrocarbons in soil - SFE versus soxhlet and water effect on recovery." *International Journal of Environmental Analytical Chemistry*, 60 (2-4), 123-137.

Hawari, J., Halasz, A., Beiruty, A., Sas, I., and Tra, H. V. (1997). "Practicality of supercritical fluid extraction IR for the measurement of petroleum hydrocarbons in aged soil: A comparative study between two commercial extractors." *International Journal of Environmental Analytical Chemistry*, 66 (4), 299-311.

Hawthorne, S. B., and Grabanski, C. B. (2000). "Correlating selective supercritical fluid extraction with bioremediation behavior of PAHs in a field treatment plot." *Environmental Science and Technology*, 34, 4103-4110.

Hawthorne, S. B., Grabanski, C. B., Martin, E., and Miller, D. J. (2000). "Comparisons of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction and subcritical water extraction for environmental solids: recovery, selectivity and effects on sample matrix." *Journal of Chromatography A*, 892 (1-2), 421-433.

Hawthorne, S. B., Lagenfeld, J. J., Miller, D. J., and Burford, M. D. (1992). "Comparison of supercritical $CHCLF_2$, N_2O, and CO_2 for the extraction of polychlorinated biphenyls and polycyclic aromatic hydrocarbons." *Analytical Chemistry*, 64 (14), 1614-1622.

Hedrick, J., Mulcahey, L. J., and Taylor, L. T. (1992). "Supercritical fluid extraction." *Microchemica Acta*, 108, 115-132.

Hess, R. K., Erkey, C., and Akgerman, A. (1991). "Supercritical extraction of phenol from soil." *Journal of Supercritical Fluids*, 4 (1), 47-52.

Howdle, S. (2002). "Supercritical fluids: a clean route to polymer synthesis and polymer processing." *Green Chemistry*, 4 (3), G29-G31.

Hwang, J., Park, S. J., Deo, M. D., and Hanson, F. V. (1995). "Phase-behavior of CO_2 crude-oil mixtures in supercritical-fluid extraction system - experimental-data and modeling." *Industrial & Engineering Chemistry Research*, 34 (4), 1280-1286.

Illes, V., Szalai, O., Then, M., Daood, H., and Perneczki, S. (1997). "Extraction of hiprose fruit by supercritical CO_2 and propane." *Journal of Supercritical Fluids*, 10 (3), 209-218.

Kazarian, S. G. (2002). "Polymers and supercritical fluids: Opportunities for vibrational spectroscopy." *Macromolecular Symposia*, 184, 215-228.

Kothandaraman, S., Venkataramani, A. C., and Andrews, A. T. (1992). "Supercritical extraction of polynuclear aromatic hydrocarbons from soil." *Environmental Progress*, 11 (3), 220-222.

Laintz, K. E., Wai, C. M., Yonker, C. R., and Smith, R. D. (1992). "Extraction of metal ions from liquid and solid materials by supercritical carbon dioxide." *Analytical Chemistry*, 64 (22), 2875-2878.

Laitinen, A., Michaux, A., and Aaltonen, O. (1994). "Soil cleaning by carbon dioxide extraction: a review." *Environmental Technology*, 15, 715-727.

Langenfeld, J. J., Hawthorne, S. B., Miller, D. J., and Pawliszyn, J. (1993). "Effects of temperature and pressure on supercritical fluid extraction efficiencies of polycyclic aromatic hydrocarbons and polychlorinated biphenyls." *Analytical Chemistry*, 64 (5), 338-344.

Lee, C. M., and Gongaware, D. F. (1997). "Optimization of SFE conditions for the removal of diesel fuel." *Environmental Technology*, 18 (11), 1157-1161.

Lemmon, E. W., McLinden, M. O., and Friend, D. G. (2003). *Thermophysical properties of fluid systems. in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, March 2003,National Institute of Standards and Technology*, Gaithersburg MD, 20899 (http://webbook.nist.gov).

Levy, J. M., Storozynsky, E., and Ashraf-Khorassani, M. "Use of modifiers in supercritical fluid extraction, supercritical fluid technology." *ACS Symposium Series-488*, 336-361.

Li Jun, Davis A. Thomas, and Matthews, M. A. (2003). "Supercritical fluid extraction of 1,2,4-trichlorobenzene from DOE job contol wastes." *Separation Science and Technology*, 38 (12-13), 2979-2993.

Liang, S., and Tilotta, C. D. (2003). "Determination of total petroleum hydrocarbons in soil by dynamic on-line supercritical fluid extraction with infrared photometric detection." *Journal of Chromatograpy A*, 986, 319-325.

Liu, M. H., Kapila, S., Yanders, A. F., Clevenger, T. E., and Elseewia, A. A. (1991). "Role of entrainers in supercritical fluid extraction of chlorinated aromatics from soil." *Role of entrainers in supercritical fluid extraction of chlorinated aromatics from soil*, 23 (8-10), 1085-1095.

Lloyd, E. D. J., and George, H. H. (1994). *Soil remediation for the petroleum extraction industry*, Penn Well Publishing Company, Tulsa, Oklahoma.

Lopez Avila, V., Young, R., Kim, R., and Beckert, W. F. (1993). "Interlaboratory evaluation of an off-line supercritical-fluid etraction infrared spectrometric method for determination of petroleum hydrocarbons in solid matrices." *Journal of AOAC International*, 76 (3), 555-564.

Lopez-Avila, V., Benedicto, J., Dhodiwala, S. N., Young, R., and Beckert, W. F. (1992). "Development of an off-line SFE-IR method for petroleum hydrocarbon in soils." *Journal of Chromatographic Science*, 30, 335.

Lopez-Avila, V., and Dodhiwala, N. S. (1990). "Method for the supercritical fluid extraction of soils/sediments." *U.S Environmental Protection Agency*, EPA/600/4-90/026.

Low, G. K. C., and Duffy, G. J. (1995). "Supercritical fluid extraction of petroleum hydrocarbons from contaminated soils." *Trac-Trends in Analytical Chemistry*, 14 (5), 218-225.

Madsen, E. L. (1991). "Determining in situ biodegradation: facts and challenges." *Environmental Science and Technology*, 25 (10), 1663-1673.

Marr-Liang, T., and Severson-Baker, C. (1999). "Beyond eco-terrorism: The deeper issues affecting Alberta's oilpatch." The Pembina Institute for Appropriate Development, Drayton Valley, Alberta.

McHugh, M. A., and Krukonis, V. J. (1994). *Supercritical fluid extraction: principles and practice*, Butterworth-Heinemann., Boston.

McNair, H. M., and Frazier, J. O. (1991). "SFE of environmentally relevant compounds with capillary GC detection." *American Laboratory*, 24D-24L.

Miller, K. G., Poole, C. F., and Chichila, T. M. P. (1995). "Solvent-assisted supercritical-fluid extraction for the isolation of semivolatile flavor compounds from the cinnamons of commerce and their separation by series-coupled column gas-chromatography." *Hrc-Journal of High Resolution Chromatography*, 18 (8), 461-471.

Monserrate, M., and Olesik, S. V. (1997). "Evaluation of SFE-CO_2 and methanol-CO_2 mixtures for the extraction of poly aromatic hydrocarbons from dust." *Journal of Chromatographic Science*, 35 (2), 82-90.

Morselli, L., Setti, L., Iannuccilli, A., Maly, S., Dinelli, G., and Quattroni, G. (1999). "Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil." *Journal of Chromatography A*, 845 (1-2), 357-363.

NRTEE. (1997). *Contaminated site issues in Canada*, Renouf Publishing Co. Ltd., Ottawa, Ontario.

Odusanya, O. O. (2003). "Supercritical carbon dioxide treatment of oil contaminated drill cuttings." Edmonton, Alberta, University of Alberta.

Peake, E., *et.al.* (1985). "Land treatment for the disposal of oily waste sludges." Canadian Petroleum Association., Calgary, Alberta.

Peker, H., Srinivasan, M. P., Smith, J. M., and McCoy, B. J. (1992). "Caffeine Extraction Rates from Coffee Beans with Supercritical Carbon-Dioxide." *AIChE Journal*, 38 (5), 761-770.

Peusch, M., MullerSeitz, E., Petz, M., Muller, A., and Anklam, E. (1997). "Extraction of capsaicinoids from chillies (Capsicum frutescens L) and paprika (Capsicum annuum L) using supercritical fluids and organic solvents." *Zeitschrift Fur Lebensmittel-Untersuchung Und-Forschung a-Food Research and Technology*, 204 (5), 351-355.

Phelps, L., Smart, G. and Wai, C. M. (1996). "Past, present, and possible future applications of supercritical fluid extraction technology." *Journal of Chemical Education*, 73 (12), 1163-1168.

Potter, T. L., Calabrese, E. J., and Kostecki, P. T. (1993). *Principles and practices for petroleum contaminated soils*, Lewis Publishers, Boca Raton, FL.

PTAC. (2003). "A re-evaluation of the toxicity of CCME petroleum hydrocarbon fraction F3 and interaction effects between fractions." P-talk - Newsletter, 6.

Ramalakshmi, K., and Raghavan, B. (1999). "Caffeine in coffee: Its removal. Why and how?" *Critical Reviews in Food Science and Nutrition*, 39 (5), 441-456.

Riser-Roberts, E. (1998). *Remediation of petroleum contaminated soils : biological, physical, and chemical processes*, Lewis Publishers, Boca Raton, FL.

Rost, H., Loibner, P. A., Hasinger, M., Braun, R., and Szolar, J. H. O. (2002). "Behavior of PAHs during cold storage of historically contaminated soil samples." *Chemosphere*, 49, 1239-1246.

Rowell, M. J., Ashworth, J., and Qureshi, A. A. (1992). "Bioremediation of petroleum hydrocarbons in soil environments." Environment Canada, Environmental Protection Directorate, River Road Environmental Technology Centre, Ottawa, Ontario.

Rudzinski, W. E., and Aminabhavi, T. M. (2000). "A review on extraction and identification of crude oil and related products using supercritical fluid technology." *Energy & Fuels*, 14 (2), 464-475.

Savoie, N. (2002). "Supercritical fluid extraction (SFE) of metals from soil." University of Alberta, Edmonton, Alberta,.

Schleussinger, A., Ohlmeir, B., Reiss, I., and Schulz, S. (1996). "Moisture effects on cleanup of PAH contaminated soil with dense carbon dioxide." *Environmental Science and Technology*, 30 (11), 3199-3204.

Schulz, S., and SchleuBinger, A. (1995). "Supercritical fluid extraction of contaminants from soil with a pilot plant." *Contaminated Soil '95*, 1353-1354.

Sherwood, L. "Remediation of Hydrocarbon Contaminated Soils in the Petroleum and Petrochemical Industry Using a Mobile Thermal Desorption System." *7th Annual Calgary Environmental Conference'94*, Calgary, Alberta.

Smart, N., Wai, C., and Phelps, C. (1998). "Supercritical solutions." *Chemistry in Britain*, 34 (8), 34-36.

Speer, J. (1999). "Flare pit Waste in Western Canada: Characterization mechanism to enhance flare pit sludge remediation efficiency," M.Sc. Thesis, University of Calgary, Calgary, Alberta.

Stiver, W., and Rampley, G. (2001). "Supercritical fluid solubility modeling." University of Guelph, Guelph, 27p.

Tomasko, D. L., Macnaughton, S. J., Foster, N. R., and Eckert, C. A. (1995). "Removal of pollutants from solid matrices using supercritical fluids." *Separation Science and Technology*, 30 (7-9), 1901-1915.

Udayasankar, K., Manohar, B., and Chokkalingam, A. (1986). "A Note on Supercritical Carbon-Dioxide Decaffeination of Coffee." *Journal of Food Science and Technology-Mysore*, 23 (6), 326-328.

USEPA. (1996). "Method 8015B: Nonhalogenated Organics Using GC/FID." United States Environmental Protection Agency, Office of Solid Waste, Washington, DC.

Valcarcel, M., and Tena, M. T. (1997). "Applications of supercritical fluid extraction in food analysis." *Fresenius Journal of Analytical Chemistry*, 358 (5), 561-573.

Vanwasen, U., Swaid, I., and Schneider, G. M. (1980). "Physicochemical principles and applications of supercritical fluid chromatography (SFC)." *Angewandte Chemie-International Edition in English*, 19 (8), 575-587.

Wenclawiak, B., Ratham, C., and Teuber, A. (1992). "Supercritical fluid extraction of soil samples and determination of Polycyclic aromatic hydrocarbons (PAHs) by HPLC." *Fresenius Journal of Analytical Chemistry*, 344 (10-11), 497-500.

Wotherspoon, E. A. a. D. B. (1989). "Petroleum industry waste mangement startegy. Overview report." Canadian Petroleum Association, Calgary, Alberta.

Wright, C. W., Wright, B. W., and Fruchter, F. (1989). "Supercritical fluid extraction of coal tar contaminated soil samples." *Energy and Fuel*, 34 (4), 374-480.

Yu, X., Wang, X., Bartha, R., and Rosen, J. D. (1990). "Supercritical extraction of coal tar contaminated soil." *Environmental Science & Technology*, 24 (11), 1732-1738.

APPENDIX A

APPENDIX A 1

Appendix A1: Sample calculations for RFs, RFavg, and F2, F3 and F4 fraction of PHCs

Based on the equations form (1) to (5) described in Section 3.2.3.2, RFs, RFavg and PHC fractions F2, F3 and F4 were calculated. Equation 1 as described in Section 3.2.3.2 is used to calculate the RF value for each concentration and the respective area obtained as shown in the sample calculation for RF value for 10.23ppm (0.000001023g/mL) nC10 calibration standard (see Table A2-1) below:

RF = Area/Concentration

⇒ 44635/0.00001023 = 4363147605

Similarly, RF values for each concentration for nC10, nC16 and nC34 were calculated. The values of various RF values are shown in Table A2-1, Table A2-2 and Table A2-3. Being 7-point calibration curve, the total number of RFs calculated for the three n-alkanes at all concentrations from 10ppm to 5000ppm are 21. All these RFs were then averaged to get an average response factor, RFavg that was used for future calculations for PHCs fractions F2, F3, and F4 as shown below

RFavg (method 1) = Sum of all the 21 individual RF values/ 21 = **3564859483**

RFavg (method 2) = Sum of all the 21 individual RF values/ 21 = **1709270793**

Now, this value is used in the calculations of fractions of PHCs:

e.g. for F2, C10-C16 hydrocarbons (mg/Kg) $= \dfrac{A_{C10\text{-}C16} \times Vol \times F}{RF_{avg} \times W_d}$

Where,

$A_{C10\text{-}C16}$ = the integration of all area counts from the apex of the nC10 peak to the apex of the nC16 peak.

Vol = Final volume of sample extract (mL)

F = Dilution factor applied to bring the samples and standards into appropriate peak height range

RF_{avg} = Average response factor calculated above

Wd = Dry weight of sample taken (g)

(Moisture content of flare pit soil 1 is 9.05%, so dry weight is 0.0905 × actual amount of soil taken for soxhlet extraction)

Sample calculation for one of the injections result obtained on 07-Aug-03 (24.1MPa, 40°C) for flare pit soil 1:

$A_{C10\text{-}C16} = 329$

Vol = 2.66 mL

RFavg = 1709270793

Dilution factor of 40 was used (0.25 mL extract (out of 2.66mL) diluted in 10mL toluene)

Wd = 5.0109 g (= 9% of the actual amount of soil taken for soxhlet extraction i.e. 5.5107*0.0905 = 5.0109g)

$$\textbf{F2, C10-C16 HCs (mg/Kg)} = \frac{329 \times 2.66\text{mL} \times 40 \times 1000000}{1709270793\text{mL/g} \times 5.0109\text{g}} = \textbf{4.09 mg/Kg}$$

Similarly, calculations for F3 and F4 fractions were done:

$$\textbf{F3, C16-C34 HCs (mg/Kg)} = \frac{32156 \times 2.66\text{mL} \times 40 \times 1000000}{1709270793\text{mL/g} \times 5.0109\text{g}} = \textbf{399.46 mg/Kg}$$

$$\textbf{F4, C34-C50 HCs (mg/Kg)} = \frac{270544 \times 2.66\text{mL} \times 40 \times 1000000}{1709270793\text{mL/g} \times 5.0109\text{g}} = \textbf{3360.86 mg/Kg}$$

Similar calculations for the results obtained from triplicate injections for each of the three sub-samples were done, and averaged. It is this averaged concentration of PHCs obtained for each fraction, which was used to calculate the % extraction efficiency of each of the individual fraction of PHCs. Based on the level of contamination of flare pit soil 1 with total PHCs being 313744 mg/kg, F2, F3 and F4 fraction corresponded to 3300mg/Kg, 17000mg/Kg and 12000 mg/kg respectively (see Table 3.1). Following below are the calculations for extraction efficiency of individual HCs. The average F2, F3 and F4 fraction of PHCs present in the three sub-samples of SC CO_2 extraction Run 1 performed on 07-Aug-03 at 24.1MPa, 40°C are sown below (see Table 4.10):

Average F2 = 11.35 mg/Kg

Extraction efficiency (%) = (3300mg/Kg-11.35mg/Kg)*100/3300mg/Kg = **99.66%**

Average F3 = 407.61 mg/Kg

Extraction efficiency (%) = (17000mg/Kg-407.61mg/Kg)*100/17000mg/Kg = **97.60%**

Average F4 = 2943.02 mg/Kg

Extraction efficiency (%) = (12000mg/Kg-2943mg/Kg)*100/12000mg/Kg = **75.47%**

Appendix A2: n-alkane Calibration Standards (Method1)

Table A2-1: n-alkane (nC10) Calibration Standards (Method1)

n-Alkane (nC10) calibration standard (ppm)		Corrected Chromatogram Area for nC10	RFs	nC10 RFavg.
Nominal Concentration	Actual Concentration			
10	10.23	44635	4363147605	
100	102.3	291252	2847038123	
500	511	1456264	2849831050	
1000	1023	3799230	3713812643	3403906176
2000	2045	7376620	3607148981	
3000	3185	10259851	3221303297	
5000	5309	17121852	3225061531	
15*	15	66715	4447666667	

*nC50 – 15ppm retention time standard and response factor

The actual concentration was plotted against the corrected chromatogram area, as shown in Figure 4.13 for calibration curves obtained for nC10, nC16 and nC34.

Table A2-2: n-alkane (nC16) Calibration Standards (Method 1)

n-Alkane (nC16) calibration standard (ppm)				
Nominal Concentration	Actual Concentration	Corrected Chromatogram Area for nC16	RFs	nC15 RFavg.
10	10.65	36406	3418435055	
100	106.5	329911	3097755869	
500	532	1741988	3274413534	
1000	1065	3633615	3411845070	3492329420
2000	2130	8278419	3886581690	
3000	3444	12760379	3705104336	
5000	5740	20963458	3652170383	

Table A2-3: n-alkane (nC34) Calibration Standards (Method 1)

n-Alkane (nC34) calibration standard (ppm)		Corrected Chromatogram Area for nC16	RFs	nC34 RFavg.
Nominal Concentration	Actual Concentration			
10	10.46	36661	3504907584	3798342853
100	104.6	394915	3775474825	
500	520	1963691	3776329487	
1000	1046	4508602	4310326721	
2000	2032	7518656	3700126148	
3000	3123	11594370	3712574448	
5000	5080	19347997	3808660761	

APPENDIX B

Appendix B: Sample spreadsheet of SC CO_2 extraction experiment data

Date: 2003-08-03

Filename: 2003-08-03 20.7 MPa, 40 °C, double cycle extraction

Comments: 50.0282 g of contaminated flare pit soil 1, at 20.7 MPa, 40°C, double cycle. A and B already refilled and pressurized to 20.7MPa. Pump B opened to vessel 331 s. 1st Static started at 710 s. Pump B stopped, refilled and repressurized to 20.7MPa at 980s s. 1st Static ends (1st dynamic starts) at 4361s. 1st Dynamic ends (2nd static starts) at 62815 s. Pump B stopped, refilled and repressurized again during 2nd static at 6371s. Opened to vessel at 65115 s. 2nd static ends (2nd dynamic starts) at 97815 s. 2nd dynamic ends at 115605 s. double cycle extraction ends. LabView stopped at 12800s.

Time (s)	Pump pressure (MPa)			Pressure Transducer (MPa)	Pump flow (mL/min)			Temperature (°C)
	Pump A	Pump B	Total		Pump A	Pump B	Total	
Start of run. LabView data acquisition started, both pumps already pressurized to 20.7 MPa but not open to the vessel yet								
11	20.7	20.7	20.7	0.6	4.5	2.1	0.0	36.7
20	20.7	20.7	20.7	0.8	4.1	1.9	0.0	36.9
31	20.7	20.7	20.7	0.7	3.7	1.8	0.0	36.8
41	20.7	20.7	20.7	0.7	3.4	1.7	0.0	36.9
50	20.7	20.7	20.7	0.7	3.6	1.8	0.0	36.9
61	20.7	20.7	20.7	0.7	-1.1	1.2	0.0	37.0
71	20.7	20.7	20.7	0.7	2.8	1.7	0.0	40.9
80	20.7	20.7	20.7	0.8	2.5	1.3	0.0	43.0
91	20.7	20.7	20.7	0.7	2.3	1.3	0.0	43.2
101	20.7	20.7	20.7	1.1	2.2	1.2	0.0	43.3
110	20.7	20.7	20.7	0.6	2.0	1.2	0.0	43.3
121	20.7	20.7	20.7	0.9	1.9	1.1	0.0	43.0
131	20.7	20.7	20.7	1.1	1.8	1.1	0.0	43.1
140	20.7	20.7	20.7	0.8	1.7	1.0	0.0	43.1
151	20.7	20.7	20.7	0.7	1.6	1.0	0.0	43.0
161	20.7	20.7	20.7	0.7	1.6	1.0	0.0	43.1
170	20.7	20.7	20.7	0.9	1.5	0.9	0.0	43.0
181	20.7	20.7	20.7	0.8	1.4	0.9	0.0	42.9
191	20.7	20.7	20.7	0.7	1.4	0.8	0.0	42.9

200	20.7	20.7	20.7	0.6	1.3	0.8	0.0	42.9
211	20.7	20.7	20.7	0.7	1.3	0.7	0.0	42.9
221	20.7	20.7	20.7	0.6	1.2	0.5	0.0	42.8
230	20.7	20.7	20.7	0.7	1.2	0.5	0.0	42.7
241	20.7	20.7	20.7	0.7	1.1	0.5	0.0	42.5
251	20.7	20.7	20.7	0.8	1.1	0.5	0.0	42.4
260	20.7	20.7	20.7	0.4	1.1	0.6	0.0	42.2
271	20.7	20.7	20.7	0.8	1.0	0.6	0.0	42.0
281	20.7	20.7	20.7	0.7	1.0	-0.2	0.0	41.8
290	20.7	20.7	20.7	1.0	0.1	0.4	0.0	41.8
301	20.7	20.7	20.7	0.8	1.0	0.5	0.0	41.5
311	20.7	20.7	20.7	0.7	0.9	0.5	0.0	41.5
320	20.7	20.2	20.7	0.7	0.9	0.5	0.0	41.3
331	20.3	19.8	20.2	11.4	63.8	94.0	0.0	41.2

Pressurized flow opened to vessel at 331 s

341	20.9	20.3	20.9	12.0	11.3	132.7	0.0	40.7
350	20.7	20.7	20.7	12.7	0.1	139.4	0.0	39.2
361	20.7	20.7	20.7	13.2	0.3	133.2	0.0	36.3
371	20.7	20.7	20.7	13.6	0.4	130.4	0.0	37.8
380	20.7	20.7	20.7	13.9	0.4	127.5	0.0	39.4
391	20.7	20.7	20.7	14.4	0.5	123.0	0.0	41.2
401	20.7	20.7	20.7	15.0	0.5	115.3	0.0	42.9
410	20.7	20.7	20.7	16.4	0.5	103.3	0.0	44.8
421	20.7	20.7	20.7	18.3	0.5	79.8	0.0	46.3
431	20.7	20.7	20.7	20.1	0.5	50.7	0.0	47.1
440	20.7	20.7	20.7	21.0	0.5	24.9	0.0	46.8
451	20.7	20.7	20.7	21.2	0.5	9.4	0.0	45.6
461	20.7	20.7	20.7	21.3	0.5	5.9	0.0	44.6
470	20.7	20.7	20.7	21.2	0.5	4.4	0.0	43.8
481	20.7	20.7	20.7	21.3	0.5	3.2	0.0	43.3
491	20.7	20.7	20.7	21.3	0.5	2.5	0.0	42.9
500	20.7	20.7	20.7	21.3	0.5	1.8	0.0	42.6
511	20.7	20.7	20.7	21.3	0.5	1.2	0.0	42.3
521	20.7	20.7	20.7	21.3	0.5	1.0	0.0	42.2
530	20.7	20.7	20.7	21.3	0.5	0.9	0.0	42.0
541	20.7	20.7	20.7	21.3	0.5	0.7	0.0	41.8
551	20.7	20.7	20.7	21.3	0.5	0.5	0.0	41.8
560	20.7	20.7	20.7	21.3	0.5	0.5	0.0	41.6
571	20.7	20.7	20.7	21.3	0.5	0.4	0.0	41.6
581	20.7	20.7	20.7	21.3	0.5	0.4	0.0	41.5
590	20.7	20.7	20.7	21.3	0.4	0.2	0.0	41.5
601	20.7	20.7	20.7	21.1	0.4	0.1	0.0	41.5
611	20.7	20.7	20.7	21.2	0.4	0.2	0.0	41.4
620	20.7	20.7	20.7	21.2	0.4	0.1	0.0	41.4

631	20.7	20.7	20.7	21.3	0.4	0.1	0.0	41.2
641	20.7	20.7	20.7	21.3	0.4	0.7	0.0	41.3
650	20.7	20.7	20.7	21.3	0.4	0.1	0.0	41.3
661	20.7	20.7	20.7	21.3	0.4	1.5	0.0	41.2
671	20.7	20.7	20.7	21.3	0.4	1.2	0.0	41.0
680	20.7	20.7	20.7	21.3	0.4	0.9	0.0	40.9
691	20.7	20.7	20.7	21.3	0.3	0.7	0.0	40.8
701	20.7	20.7	20.7	21.3	0.3	0.5	0.0	40.6
710	20.7	20.7	20.7	21.3	0.3	0.6	0.0	40.5

Started 1st Static extraction at 710s

721	20.7	20.7	20.7	21.3	0.3	0.5	0.0	40.5
731	20.7	20.7	20.7	21.3	0.3	0.4	0.0	40.5
740	20.7	20.7	20.7	21.3	0.3	0.4	0.0	40.4
751	20.7	20.7	20.7	21.3	0.3	0.2	0.0	40.4
761	20.7	20.7	20.7	21.3	0.3	0.3	0.0	40.3
770	20.7	20.7	20.7	21.3	0.3	0.2	0.0	40.3
781	20.7	20.7	20.7	21.3	0.3	0.2	0.0	40.3
791	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.2
800	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.2
811	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.2
821	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.1
[illegible]	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.1
841	20.7	20.7	20.7	21.2	0.2	0.1	0.0	40.2
851	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.2
860	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.1
871	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.2
881	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.1
890	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
901	20.7	20.7	20.7	21.2	0.2	0.1	0.0	40.0
911	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
920	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
931	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
941	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
950	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.0
961	20.7	20.7	20.7	21.3	0.2	0.0	0.0	40.0
971	20.7	20.7	20.7	21.3	0.2	0.0	0.0	40.0
980	20.7	6.3	20.7	21.3	0.2	-204.0	0.0	40.0

All valves are shut and Pump B is stopped and refilled at 980s

991	20.7	6.2	20.7	21.3	0.2	-203.5	0.0	40.0
1001	20.7	6.2	20.7	21.3	0.2	-204.0	0.0	39.9
1010	20.7	6.2	20.7	21.3	0.2	-204.1	0.0	40.0
1021	20.7	6.2	20.7	21.2	0.2	-204.1	0.0	40.0

1031	20.7	6.2	20.7	21.2	0.2	-204.1	0.0	39.9
1040	20.7	6.2	20.7	21.2	0.2	-204.1	0.0	39.9
1051	20.7	6.2	20.7	21.2	0.2	-204.0	0.0	39.9
1061	20.7	6.2	20.7	21.2	0.2	0.0	0.0	39.9
1070	20.7	6.2	20.7	21.2	0.2	0.0	0.0	40.0
1081	20.7	6.3	20.7	21.2	0.2	0.0	0.0	40.0
1091	20.7	6.3	20.7	21.2	0.2	0.0	0.0	40.0
1100	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.0
1111	20.7	6.3	20.7	21.3	0.1	0.0	0.0	40.0
1121	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.0
1130	20.7	6.3	20.7	21.3	0.1	0.0	0.0	40.0
1141	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.0
1151	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.1
1160	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.0
1171	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.0
1181	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.0
1190	20.7	6.3	20.7	21.3	0.0	0.0	0.0	40.0
1201	20.7	6.3	20.7	21.2	-0.2	0.0	0.0	40.0
1211	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1220	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.1
1231	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1241	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1250	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1261	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.1
1271	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1280	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1291	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.0
1301	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.1
1310	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.1
1321	20.7	6.3	20.7	21.1	-0.1	0.0	0.0	40.0
1331	20.7	6.3	20.7	21.2	-0.1	0.0	0.0	40.1
1340	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.1
1351	20.7	6.3	20.7	21.1	0.0	0.0	0.0	40.0
1361	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.1
1370	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.0
1381	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.2
1391	20.7	6.3	20.7	21.1	-0.1	0.0	0.0	40.0
1400	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.1
1411	20.7	6.3	20.7	21.2	0.0	0.0	0.0	40.1
1421	20.7	6.3	20.7	21.1	0.0	0.0	0.0	40.1
1430	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.1
1441	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1450	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1460	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1471	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.0
1480	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.1

1490	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.1
1501	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.2
1511	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.0
1520	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1530	20.7	6.3	20.7	21.2	0.1	0.0	0.0	40.1
1541	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1550	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1560	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1589	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1590	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1592	20.7	6.3	20.7	21.1	0.2	0.0	0.0	40.1
1600	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1610	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1620	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1630	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1641	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1651	20.7	6.3	20.7	21.0	0.1	0.0	0.0	40.2
1661	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1670	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.1
1681	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1691	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1700	20.7	6.3	20.7	21.0	0.1	0.0	0.0	40.2
1711	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1721	20.7	6.3	20.7	21.1	0.1	0.0	0.0	40.2
1730	20.7	6.3	20.7	21.0	0.2	0.0	0.0	40.2
1741	20.7	6.3	20.7	21.0	0.2	0.0	0.0	40.2
1751	20.7	6.3	20.7	21.1	0.2	0.0	0.0	40.2
1760	20.7	10.2	20.7	21.1	0.2	191.2	0.0	40.2

Pump B opened to the vessel at 1760 s

1771	20.7	19.4	20.7	21.0	0.2	50.5	0.0	40.2
1781	20.7	20.5	20.7	21.1	0.1	27.1	0.0	40.1
1790	20.7	20.7	20.7	21.1	0.1	14.3	0.0	40.3
1801	20.7	20.7	20.7	21.1	0.1	8.3	0.0	40.3
1811	20.7	20.7	20.7	21.0	0.1	6.2	0.0	40.2
1820	20.7	20.7	20.7	21.0	0.1	5.3	0.0	40.1
1831	20.7	20.7	20.7	21.1	0.1	4.2	0.0	40.3
1841	20.7	20.7	20.7	21.1	0.1	3.5	0.0	40.2
1850	20.7	20.7	20.7	21.0	0.0	3.1	0.0	40.2
1860	20.7	20.7	20.7	21.0	0.0	2.8	0.0	40.2
1871	20.7	20.7	20.7	21.1	0.0	2.5	0.0	40.2
1880	20.7	20.7	20.7	21.1	0.0	2.3	0.0	40.2
1890	20.7	20.7	20.7	21.0	0.0	2.2	0.0	40.2
1901	20.7	20.7	20.7	21.1	-0.6	2.0	0.0	40.3
1910	20.7	20.7	20.7	21.0	0.0	1.9	0.0	40.3

1920	20.7	20.7	20.7	21.1	-0.2	1.8	0.0	40.2
1931	20.7	20.7	20.7	21.1	-0.2	1.7	0.0	40.2
1940	20.7	20.7	20.7	21.1	-0.2	1.6	0.0	40.2
1950	20.7	20.7	20.7	21.1	-0.3	1.5	0.0	40.3
1961	20.7	20.7	20.7	21.1	-0.3	1.5	0.0	40.2
1971	20.7	20.7	20.7	21.1	-0.3	1.4	0.0	40.2
1980	20.7	20.7	20.7	21.1	-0.3	1.4	0.0	40.2
1990	20.7	20.7	20.7	21.1	-0.3	1.3	0.0	40.3
2001	20.7	20.7	20.7	21.1	-0.3	1.3	0.0	40.2
2010	20.7	20.7	20.7	21.1	-0.3	1.2	0.0	40.3
2020	20.7	20.7	20.7	21.1	-0.3	1.2	0.0	40.2
2030	20.7	20.7	20.7	21.1	-0.1	1.1	0.0	40.3
2041	20.7	20.2	20.7	21.1	-0.2	9.7	0.0	40.3

Bypassing pure SC CO_2 through the lines down stream of the vessel and adjusting metering valve flow rate to 10mL/min (average)

2051	20.7	20.8	20.7	21.1	-0.7	2.2	0.0	40.3
2060	20.7	20.7	20.7	21.0	-0.7	7.1	0.0	40.3
2071	20.7	20.7	20.7	21.0	-0.1	9.6	0.0	40.3
2081	20.7	20.7	20.7	21.1	-0.2	9.3	0.0	40.3
2090	20.7	20.7	20.7	21.0	-0.2	8.6	0.0	40.3
2101	20.7	20.7	20.7	21.0	-0.2	10.5	0.0	40.3
2111	20.7	20.7	20.7	21.0	-0.1	9.5	0.0	40.3
2120	20.7	20.7	20.7	21.1	-0.1	8.8	0.0	40.3
2131	20.7	20.7	20.7	21.1	-0.1	1.0	0.0	40.3
2141	20.7	20.7	20.7	21.1	-0.1	0.5	0.0	40.3
2150	20.7	20.7	20.7	21.1	-0.1	0.5	0.0	40.2
2161	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2171	20.7	20.7	20.7	21.1	-0.1	0.5	0.0	40.3
2180	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2191	20.7	20.7	20.7	21.0	0.0	0.5	0.0	40.2
2201	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.2
2210	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2220	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2231	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2240	20.7	20.7	20.7	21.1	0.0	0.5	0.0	40.3
2250	20.7	20.7	20.7	21.1	0.2	0.4	0.0	40.3
2261	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.4
2270	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2280	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2291	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2301	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2310	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.2
2321	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2330	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3

2340	20.7	20.7	20.7	21.1	0.1	0.4	0.0	40.3
2351	20.7	20.7	20.7	21.1	0.1	0.3	0.0	40.3
2360	20.7	20.7	20.7	21.1	0.1	0.3	0.0	40.3
2370	20.7	20.7	20.7	21.1	0.1	0.3	0.0	40.3
2381	20.7	20.7	20.7	21.1	0.1	0.3	0.0	40.3
2390	20.7	20.7	20.7	21.2	0.1	6.9	0.0	40.3
2400	20.7	20.7	20.7	21.3	0.2	0.9	0.0	40.4
2411	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.4
2421	20.7	20.7	20.7	21.3	0.2	0.5	0.0	40.4
2430	20.7	20.7	20.7	21.2	0.2	0.6	0.0	40.4
2440	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.3
2451	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2461	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.4
2470	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.3
2481	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.3
2491	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2500	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2511	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.3
2521	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.3
2530	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.4
2541	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2551	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2560	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2571	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2581	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2590	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2600	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.4
2611	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2620	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2630	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2641	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2651	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2660	20.7	20.7	20.7	21.3	0.2	0.1	0.0	40.3
2671	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.3
2681	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2690	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2701	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2711	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
2720	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
2731	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2741	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2750	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
2761	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2771	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2780	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
2791	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3

2801	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2811	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2821	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2830	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
2841	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
2851	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
2860	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
2871	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
2881	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2890	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2901	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
2911	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.4
2920	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2931	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2941	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2950	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.4
2961	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.3
2971	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2980	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
2991	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
3001	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3010	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3021	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3031	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3040	20.7	20.7	20.7	21.2	0.1	0.3	0.0	40.4
3051	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3061	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3070	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3081	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
3091	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3100	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3111	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3121	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3130	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.4
3141	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3151	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3160	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3171	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
3181	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3190	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
3201	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3211	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3220	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3230	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.3
3241	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3251	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4

3261	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.4
3270	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3281	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
3291	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3300	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
3311	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3321	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3330	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
3341	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3351	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
3360	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3371	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3381	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3390	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3401	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3411	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
3420	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.3
3430	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3441	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.4
3450	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3460	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
3471	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.3
3480	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
3490	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3501	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3510	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3520	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3531	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.3
3541	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3550	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3561	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
3571	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3580	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3591	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.3
3601	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3610	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3621	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3631	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
3640	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
3651	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3661	20.7	20.7	20.7	21.2	0.1	0.0	0.0	41.6
3670	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.3
3681	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.3
3691	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
3700	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
3711	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4

3721	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
3730	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3741	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.4
3751	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.3
3760	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
3770	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
3780	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
3791	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3800	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
3810	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
3821	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3831	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3840	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
3851	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
3861	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3870	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3881	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
3891	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.3
3900	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
3911	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3921	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3930	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3941	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
3951	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
3960	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3971	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
3981	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
3990	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
4001	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4011	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4020	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4031	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
4041	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.6
4050	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4061	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.3
4071	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
4080	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
4091	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.3
4101	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
4110	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4121	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4131	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
4140	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4151	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
4161	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4170	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4

4181	20.7	20.7	20.7	21.3	0.0	0.0	0.1	40.5
4191	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.3
4200	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4211	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
4221	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
4230	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4240	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
4251	20.7	20.7	20.7	21.4	0.0	0.0	0.0	40.4
4261	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
4270	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
4281	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.3
4291	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4300	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4311	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
4321	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
4330	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
4340	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
4351	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
4361	20.6	20.2	20.7	20.7	0.0	14.6	0.3	40.4

Started 1st dynamic extraction at 4361 s with SC CO_2 flow rate of 10mL/min (average)

4370	20.7	20.7	20.7	21.3	0.3	5.7	0.8	40.3
4381	20.7	20.7	20.7	21.3	0.0	2.1	0.4	40.5
4391	20.7	20.7	20.7	21.3	0.0	4.7	5.0	40.4
4401	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.4
4410	20.7	20.7	20.7	21.2	0.0	10.4	5.0	40.3
4421	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
4431	20.7	20.7	20.7	21.2	0.0	8.2	5.0	40.4
4440	20.7	20.7	20.7	21.3	0.0	7.8	5.0	40.4
4451	20.7	20.7	20.7	21.2	0.0	11.4	5.0	40.3
4461	20.7	20.7	20.7	21.2	0.0	10.9	5.0	40.4
4470	20.7	20.7	20.7	21.2	0.0	10.8	5.0	40.3
4481	20.7	20.7	20.7	21.2	0.0	9.6	5.0	40.3
4491	20.7	20.7	20.7	21.3	0.0	8.0	5.0	40.3
4501	20.7	20.7	20.7	21.3	0.0	6.5	5.0	40.3
4511	20.7	20.7	20.7	21.3	0.0	6.2	5.0	40.4
4520	20.7	20.7	20.7	21.2	0.0	6.2	5.0	40.4
4530	20.7	20.7	20.7	21.3	0.0	6.3	5.0	40.4
4541	20.7	20.7	20.7	21.2	0.0	5.9	5.0	40.3
4550	20.7	20.7	20.7	21.3	0.0	6.2	5.0	40.3
4560	20.7	20.7	20.7	21.3	0.0	6.6	5.0	40.4
4571	20.7	20.7	20.7	21.3	0.0	6.6	5.0	40.4
4580	20.7	20.7	20.7	21.3	0.0	6.2	5.0	40.3
4590	20.7	20.7	20.7	21.3	0.0	6.5	5.0	40.3
4601	20.7	20.7	20.7	21.3	0.0	6.6	5.0	40.4

4610	20.7	20.7	20.7	21.2	0.0	8.4	5.0	40.5
4620	20.7	20.7	20.7	21.3	0.0	11.0	5.0	40.3
4631	20.7	20.7	20.7	21.2	0.0	11.8	5.0	40.3
4640	20.7	20.7	20.7	21.2	0.0	11.6	5.0	40.3
4650	20.7	20.7	20.7	21.3	0.0	11.1	5.0	40.3
4661	20.7	20.7	20.7	21.3	0.0	10.0	5.0	40.3
4670	20.7	20.7	20.7	21.2	0.0	10.0	0.8	40.3
4680	20.7	20.7	20.7	21.3	0.0	10.3	5.0	40.4
4691	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.3
4700	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
4710	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
4721	20.7	20.7	20.7	21.3	0.0	10.0	5.0	40.3
4730	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
4740	20.7	20.7	20.7	21.3	0.0	9.1	5.0	40.3
4751	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
4760	20.7	20.7	20.7	21.2	0.0	9.0	5.0	40.3
4770	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
4781	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.3
4791	20.7	20.7	20.7	21.2	0.0	10.3	5.0	40.3
4800	20.7	20.7	20.7	21.2	0.0	10.0	5.0	40.4
4811	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.3
4821	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
4830	20.7	20.7	20.7	21.3	0.0	10.0	5.0	40.3
4841	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
4851	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
4860	20.7	20.7	20.7	21.2	0.0	11.7	5.0	40.3
4871	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.4
4881	20.7	20.7	20.7	21.3	0.0	8.6	5.0	40.3
4890	20.7	20.7	20.7	21.3	0.0	8.8	5.0	40.3
4901	20.7	20.7	20.7	21.3	0.0	9.0	5.0	40.3
4911	20.7	20.7	20.7	21.3	0.0	8.4	5.0	40.3
4920	20.7	20.7	20.7	21.2	0.0	10.1	5.0	40.3
4931	20.7	20.7	20.7	21.3	0.0	10.7	5.0	40.3
4941	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.4
4950	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
4961	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
4971	20.7	20.7	20.7	21.3	0.0	9.4	0.4	40.3
4980	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
4991	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
5001	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
5011	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
5020	20.7	20.7	20.7	21.3	0.0	8.8	5.0	40.3
5031	20.7	20.7	20.7	21.3	0.0	9.1	5.0	40.3
5041	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
5050	20.7	20.7	20.7	21.3	0.0	9.0	5.0	40.3
5061	20.7	20.7	20.7	21.3	0.0	9.0	5.0	40.3

5071	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.4
5080	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
5091	20.7	20.7	20.7	21.3	0.0	8.7	5.0	40.3
5101	20.7	20.7	20.7	21.3	0.0	9.1	5.0	40.3
5110	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.4
5120	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
5130	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
5141	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.4
5151	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.4
5161	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.3
5170	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.3
5181	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
5191	20.7	20.7	20.7	21.2	0.0	9.9	5.0	40.3
5200	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
5211	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.3
5221	20.7	20.7	20.7	21.3	0.0	11.2	5.0	40.3
5230	20.7	20.7	20.7	21.2	0.0	10.7	5.0	40.3
5241	20.7	20.7	20.7	21.2	0.0	10.4	5.0	40.3
5251	20.7	20.7	20.7	21.2	0.0	10.4	5.0	40.3
5260	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
5271	20.7	20.7	20.7	21.2	0.0	9.7	5.0	40.3
5281	20.7	20.7	20.7	21.3	0.0	9.3	0.5	40.3
5290	20.7	20.7	20.7	21.3	0.0	9.8	4.6	40.5
5301	20.7	20.7	20.7	21.2	0.0	9.9	4.5	40.4
5311	20.7	20.7	20.7	21.3	0.0	8.6	4.0	40.3
5320	20.7	20.7	20.7	21.2	0.0	8.8	4.0	40.3
5331	20.7	20.7	20.7	21.3	0.0	8.7	3.8	40.2
5341	20.7	20.7	20.7	21.3	0.0	8.2	4.2	40.3
5351	20.7	20.7	20.7	21.3	0.0	8.0	3.7	40.3
5361	20.7	20.7	20.7	21.3	0.0	8.3	3.6	40.3
5370	20.7	20.7	20.7	21.3	0.0	8.4	3.5	40.4
5381	20.7	20.7	20.7	21.3	0.0	7.9	3.7	40.3
5391	20.7	20.7	20.7	21.2	0.0	8.2	3.5	40.4
5400	20.7	20.7	20.7	21.3	0.0	8.6	4.1	40.3
5411	20.7	20.7	20.7	21.2	0.0	8.4	3.7	40.3
5421	20.7	20.7	20.7	21.3	0.0	12.8	5.0	40.3
5430	20.7	20.7	20.7	21.3	0.0	12.1	4.7	40.3
5441	20.7	20.7	20.7	21.2	0.0	11.5	4.2	40.3
5451	20.7	20.7	20.7	21.3	0.0	10.3	4.1	40.3
5460	20.7	20.7	20.7	21.3	0.0	10.6	4.3	40.3
5471	20.7	20.7	20.7	21.2	0.0	10.8	3.2	40.3
5481	20.7	20.7	20.7	21.3	0.0	8.3	3.2	40.4
5490	20.7	20.7	20.7	21.3	0.0	7.9	3.1	40.3
5501	20.7	20.7	20.7	21.3	0.0	7.9	3.2	40.3
5511	20.7	20.7	20.7	21.2	0.0	8.3	3.3	40.3
5520	20.7	20.7	20.7	21.2	0.0	8.0	3.2	40.3

5530	20.7	20.7	20.7	21.2	0.0	8.0	3.3	40.4
5541	20.7	20.7	20.7	21.3	0.0	8.6	3.5	40.4
5550	20.7	20.7	20.7	21.2	0.0	8.9	3.6	40.3
5560	20.7	20.7	20.7	21.2	0.0	8.5	1.7	40.3
5571	20.7	20.7	20.7	21.3	0.0	9.0	0.1	40.4
5580	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
5591	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
5601	20.7	20.7	20.7	21.2	0.0	8.9	5.0	40.3
5610	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
5620	20.7	20.7	20.7	21.3	0.0	9.0	5.0	40.3
5631	20.7	20.7	20.7	21.2	0.0	8.8	5.0	40.2
5640	20.7	20.7	20.7	21.2	0.0	12.9	5.0	40.3
5650	20.7	20.7	20.7	21.3	0.0	12.1	5.0	40.4
5661	20.7	20.7	20.7	21.3	0.0	12.0	5.0	40.3
5670	20.7	20.7	20.7	21.3	0.0	10.7	5.0	40.3
5680	20.7	20.7	20.7	21.2	0.0	10.8	5.0	40.3
5691	20.7	20.7	20.7	21.2	0.0	10.6	5.0	40.3
5700	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.3
5710	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
5721	20.7	20.7	20.7	21.2	0.0	9.6	5.0	40.3
5730	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.3
5741	20.7	20.7	20.7	21.2	0.0	9.0	5.0	40.3
5751	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.5
5760	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
5771	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.4
5781	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
5790	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.4
5801	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
5811	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.3
5820	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
5831	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.4
5841	20.7	20.7	20.7	21.2	0.0	11.6	5.0	40.3
5850	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.4
5861	20.7	20.7	20.7	21.2	0.0	10.0	5.0	40.3
5871	20.7	20.7	20.7	21.3	0.0	10.5	3.8	40.3
5880	20.7	20.6	20.7	21.2	0.0	12.5	5.0	40.3
5890	20.7	20.7	20.7	21.2	0.0	10.1	5.0	40.3
5901	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.3
5910	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.3
5920	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.3
5931	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.4
5941	20.7	20.7	20.7	21.2	0.0	10.1	5.0	40.3
5950	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.3
5961	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.4
5971	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
5980	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3

5991	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
6001	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.3
6010	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
6021	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.5
6031	20.7	20.7	20.7	21.2	0.0	8.9	5.0	40.3
6041	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
6050	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.3
6061	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
6071	20.7	20.7	20.7	21.3	0.0	8.9	5.0	40.3
6080	20.7	20.7	20.7	21.3	0.0	8.9	5.0	40.3
6091	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
6101	20.7	20.7	20.7	21.3	0.0	9.0	5.0	40.3
6110	20.7	20.7	20.7	21.2	0.0	14.7	5.0	40.3
6121	20.7	20.7	20.7	21.2	0.0	14.9	5.0	40.4
6131	20.7	20.7	20.7	21.2	0.0	12.3	5.0	40.3
6140	20.7	20.7	20.7	21.2	0.0	14.5	5.0	40.3
6151	20.7	20.7	20.7	21.2	0.0	15.1	5.0	40.3
6161	20.7	20.6	20.7	21.2	0.0	6.6	5.0	40.3
6170	20.7	20.7	20.7	21.3	0.0	-0.8	3.2	40.6
6181	20.7	20.7	20.7	21.3	0.0	-0.2	1.6	40.4
6191	20.7	20.7	20.7	21.3	0.0	-0.2	0.3	40.4
6200	20.7	20.7	20.7	21.4	0.0	0.0	1.7	40.4
6210	20.7	20.6	20.7	21.3	-0.3	16.2	5.0	40.4
6221	20.7	20.6	20.7	21.3	0.1	7.4	5.0	40.4
6231	20.7	20.7	20.7	21.3	0.0	5.3	5.0	40.4
6240	20.4	20.0	20.5	21.3	12.7	45.8	5.0	40.5
6251	20.7	20.7	20.7	21.3	0.7	52.7	5.0	40.4
6261	20.7	20.6	20.7	21.3	0.0	19.5	5.0	40.5
6270	20.7	20.7	20.7	21.3	0.0	11.9	5.0	40.3
6281	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.4

1st Dynamic extraction ends and 2nd Static extraction begins at 6281 s

6291	20.7	20.8	20.7	21.3	0.0	-1.8	5.0	40.5
6300	20.7	20.7	20.7	21.3	0.0	-0.3	1.1	40.6
6311	20.7	20.7	20.7	21.3	0.0	-0.2	0.7	40.5
6321	20.7	20.7	20.7	21.3	0.0	-0.2	0.3	40.4
6330	20.7	20.7	20.7	21.3	0.0	-0.2	0.2	40.4
6341	20.7	20.7	20.7	21.3	0.0	-0.2	0.2	40.5
6351	20.7	20.7	20.7	21.3	0.0	-0.1	0.2	40.5
6360	20.7	20.7	20.7	21.3	0.0	0.0	0.1	40.6
6371	20.7	6.3	20.7	21.3	0.0	-204.1	0.1	40.5

Pump B stopped, refilled and repressurized at 6371 s

6381	20.7	6.2	20.7	21.3	0.0	-204.1	0.1	40.5

6390	20.7	6.2	20.7	21.3	0.0	-203.8	0.1	40.5
6401	20.7	6.2	20.7	21.3	0.0	-204.1	0.1	40.5
6411	20.7	6.2	20.7	21.3	0.0	-203.8	0.1	40.5
6420	20.7	6.2	20.7	21.3	0.0	-204.1	0.1	40.5
6430	20.7	6.2	20.7	21.3	0.1	-204.0	0.1	40.4
6440	20.7	6.2	20.7	21.3	0.1	-203.9	0.1	40.4
6451	20.7	6.2	20.7	21.3	0.1	-204.1	0.1	40.6
6461	20.7	6.2	20.7	21.3	0.1	-204.1	0.1	40.5
6470	20.7	6.2	20.7	21.3	0.1	-204.1	0.1	40.5
6481	20.7	6.2	20.7	21.3	0.1	-204.0	0.1	40.6
6491	20.7	6.2	20.7	21.3	0.1	0.0	0.1	40.5
6500	20.7	6.3	20.7	21.3	0.1	0.0	0.0	40.4
6511	20.7	8.1	20.7	21.3	0.0	194.3	0.1	40.5

Pressurized Pump B opened to the vessel at 6511s

6521	20.7	14.9	20.7	21.3	0.0	184.8	0.0	40.5
6530	20.7	19.5	20.7	21.3	0.0	46.0	0.0	40.4
6541	20.7	20.6	20.7	21.3	0.0	29.6	0.0	40.6
6551	20.7	20.7	20.7	21.3	0.4	16.2	0.0	40.5
6560	20.7	20.7	20.7	21.3	-0.2	11.1	0.0	40.4
6571	20.7	20.7	20.7	21.4	-0.3	8.4	0.0	40.4
6581	20.7	20.7	20.7	21.3	-0.4	7.5	0.0	40.4
6590	20.7	20.7	20.7	21.3	-0.4	6.4	0.0	40.5
6601	20.7	20.7	20.7	21.3	-0.5	5.6	0.0	40.5
6611	20.7	20.7	20.7	21.3	-0.5	5.0	0.0	40.4
6620	20.7	20.7	20.7	21.3	-0.6	4.6	0.0	40.4
6631	20.7	20.7	20.7	21.3	-0.6	4.1	0.0	40.6
6641	20.7	20.7	20.7	21.3	-0.7	3.8	0.0	40.4
6650	20.7	20.7	20.7	21.3	-0.7	3.5	0.0	40.5
6661	20.7	20.7	20.7	21.3	-0.7	3.2	0.0	40.3
6671	20.7	20.7	20.7	21.3	-0.7	3.0	0.0	40.4
6680	20.7	20.7	20.7	21.3	-0.7	2.9	0.0	40.5
6691	20.7	20.7	20.7	21.3	-0.7	2.7	0.0	40.4
6701	20.7	20.7	20.7	21.3	-0.7	2.6	0.0	40.4
6710	20.7	20.7	20.7	21.3	-0.6	2.4	0.0	40.5
6721	20.7	20.7	20.7	21.3	-0.6	2.3	0.0	40.5
6731	20.7	20.7	20.7	21.3	-0.6	2.2	0.0	40.5
6740	20.7	20.7	20.7	21.3	-0.5	2.1	0.0	40.4
6751	20.7	20.7	20.7	21.3	-0.5	2.0	0.0	40.4
6761	20.7	20.7	20.7	21.3	-0.5	1.9	0.0	40.5
6770	20.7	20.7	20.7	21.3	-0.5	1.8	0.0	40.5
6781	20.7	20.7	20.7	21.3	-0.4	1.7	0.0	40.5
6791	20.7	20.7	20.7	21.3	-0.4	1.6	0.0	40.5
6800	20.7	20.7	20.7	21.3	-0.4	1.5	0.0	40.4
6811	20.7	20.7	20.7	21.3	-0.3	1.5	0.0	40.5

6821	20.7	20.7	20.7	21.3	-0.3	1.4	0.0	40.4
6830	20.7	20.7	20.7	21.3	-0.3	1.3	0.0	40.6
6841	20.7	20.7	20.7	21.3	-0.1	1.3	0.0	40.3
6851	20.7	20.7	20.7	21.3	-0.2	1.2	0.0	40.5
6860	20.7	20.7	20.7	21.3	-0.2	1.1	0.0	40.5
6871	20.7	20.7	20.7	21.3	-0.2	1.1	0.0	40.5
6881	20.7	20.7	20.7	21.3	-0.1	1.1	0.0	40.4
6890	20.7	20.7	20.7	21.3	-0.1	1.0	0.0	40.5
6901	20.7	20.7	20.7	21.3	-0.1	1.0	0.0	40.4
6911	20.7	20.7	20.7	21.3	-0.1	0.9	0.0	40.5
6920	20.7	20.7	20.7	21.3	0.0	0.9	0.0	40.4
6931	20.7	20.7	20.7	21.3	0.0	0.8	0.0	40.4
6941	20.7	20.7	20.7	21.3	0.0	0.8	0.0	40.4
6950	20.7	20.7	20.7	21.3	0.0	0.8	0.0	40.5
6960	20.7	20.7	20.7	21.3	0.0	0.7	0.0	40.4
6971	20.7	20.7	20.7	21.3	0.1	0.7	0.0	40.4
6980	20.7	20.7	20.7	21.3	0.2	0.7	0.0	40.6
6991	20.7	20.7	20.7	21.3	0.1	0.6	0.0	40.3
7001	20.7	20.7	20.7	21.2	0.1	0.6	0.0	40.4
7010	20.7	20.7	20.7	21.3	0.1	0.6	0.0	40.6
7021	20.7	20.7	20.7	21.3	0.1	0.6	0.0	40.6
7031	20.7	20.7	20.7	21.3	0.1	0.6	0.0	40.5
7040	20.7	20.7	20.7	21.2	0.1	0.5	0.0	40.3
7050	20.7	20.7	20.7	21.3	0.1	0.5	0.0	40.5
7061	20.7	20.7	20.7	21.3	0.2	0.5	0.0	40.5
7070	20.7	20.7	20.7	21.2	0.2	0.4	0.0	40.5
7080	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.5
7091	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.5
7100	20.7	20.7	20.7	21.2	0.2	0.4	0.0	40.4
7110	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.6
7121	20.7	20.7	20.7	21.3	0.2	0.4	0.0	40.4
7130	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7140	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.5
7151	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7161	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7170	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.4
7181	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.3
7191	20.7	20.7	20.7	21.3	0.2	0.3	0.0	40.5
7200	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.5
7211	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.5
7221	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7230	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.6
7241	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7251	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.5
7260	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.4
7271	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.6

7281	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.5
7290	20.7	20.7	20.7	21.2	0.2	0.4	0.0	40.5
7301	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.4
7311	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.5
7320	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.5
7331	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.5
7341	20.7	20.7	20.7	21.2	0.2	0.5	0.0	40.3
7350	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.5
7360	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.5
7371	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.4
7381	20.7	20.7	20.7	21.2	0.2	0.3	0.0	40.5
7390	20.7	20.7	20.7	21.3	0.2	0.2	0.0	40.4
7401	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.4
7411	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.5
7420	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.3
7431	20.7	20.7	20.7	21.3	0.1	0.5	0.0	40.4
7441	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7450	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.6
7461	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.6
7471	20.7	20.7	20.7	21.2	0.1	0.3	0.0	40.4
7480	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7491	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7501	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7510	20.7	20.7	20.7	21.2	0.2	0.2	0.0	40.4
7520	20.7	20.7	20.7	21.3	0.1	0.4	0.0	40.4
7531	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7540	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7550	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7561	20.7	20.7	20.7	21.2	0.1	0.4	0.0	40.4
7570	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7580	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7591	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7600	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.4
7610	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.4
7621	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7631	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7641	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7650	20.7	20.7	20.7	21.2	0.1	0.3	0.0	40.5
7661	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7671	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.6
7680	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7691	20.7	20.7	20.7	21.2	0.1	0.3	0.0	40.4
7701	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
7710	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
7721	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7731	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.5

7740	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.5
7751	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7761	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
7770	20.7	20.7	20.7	21.2	0.1	0.2	0.0	40.5
7781	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7791	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7800	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7811	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.5
7821	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7830	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7840	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7851	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
7861	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
7870	20.7	20.7	20.7	21.2	0.1	0.0	0.0	40.6
7881	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.6
7890	20.7	20.7	20.7	21.2	0.1	0.1	0.0	40.4
7900	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.6
7911	20.7	20.7	20.7	21.2	0.1	0.0	0.0	40.5
7921	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.5
7930	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7941	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
7951	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
7960	20.7	20.7	20.7	21.3	0.1	0.2	0.0	40.5
7970	20.7	20.7	20.7	21.3	0.1	0.0	0.0	40.5
7981	20.7	20.7	20.7	21.2	0.1	0.0	0.0	40.6
7991	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.5
8000	20.7	20.7	20.7	21.3	0.1	0.1	0.0	40.4
8011	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
8021	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.6
8030	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8041	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.6
8051	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8060	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8071	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8081	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
8090	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
8101	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.5
8111	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8120	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.6
8131	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8141	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.5
8150	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8161	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8171	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.6
8180	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8190	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5

8201	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8211	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8220	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8231	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8241	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8250	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.6
8261	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8271	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8280	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8291	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8301	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8310	20.7	20.7	20.7	21.1	0.0	0.1	0.0	40.5
8321	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8331	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8340	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8350	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.6
8361	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8370	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8381	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8391	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
8401	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8410	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8421	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
8431	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.6
8440	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.6
8451	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8461	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8470	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8481	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.5
8491	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8500	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.6
8510	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8521	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8530	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8541	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8551	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8560	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8570	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.6
8581	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8590	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8600	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.6
8611	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8620	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
8630	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8641	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8651	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4

8660	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
8671	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8681	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8690	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8701	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.5
8711	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
8720	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8731	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8741	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8750	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.5
8760	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8771	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
8780	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
8790	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8801	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
8810	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
8820	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8831	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
8841	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
8850	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
8861	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8871	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.6
8880	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8891	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
8901	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
8910	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8920	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8931	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.3
8941	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
8950	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
8961	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
8971	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
8980	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.3
8991	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9001	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9010	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9021	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.3
9031	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9040	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9051	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9061	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
9070	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
9081	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9091	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9100	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9111	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.5

9121	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
9130	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
9141	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9151	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.6
9160	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
9170	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9181	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9190	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9200	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
9212	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9221	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.6
9230	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
9240	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
9251	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
9260	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9270	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9281	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9291	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9300	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
9311	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9321	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9330	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9341	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
9351	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
9360	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.5
9371	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9381	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.5
9390	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.5
9401	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9411	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.6
9420	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9431	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.4
9441	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9450	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9460	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9471	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
9481	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
9490	20.7	20.7	20.7	21.3	-0.1	0.0	0.0	40.4
9501	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.6
9511	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9520	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
9531	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9541	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9550	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9561	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9571	20.7	20.7	20.7	21.2	0.0	0.2	0.0	40.5

9580	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9591	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9600	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9610	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.3
9621	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9631	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9640	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9651	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.3
9661	20.7	20.7	20.7	21.3	0.0	0.2	0.0	40.4
9670	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.3
9681	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9691	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9700	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.4
9711	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9721	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.4
9730	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9741	20.7	20.7	20.7	21.2	0.0	0.1	0.0	40.3
9751	20.7	20.7	20.7	21.3	0.0	0.1	0.0	40.4
9760	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.4
9771	20.7	20.7	20.7	21.3	0.0	0.0	0.0	40.5
9781	20.7	20.5	20.7	20.9	-1.7	30.5	1.4	39.7

2nd Static extraction ends and 2nd Dynamic extraction starts at 9781 s

9790	20.7	20.6	20.7	21.2	0.1	13.2	5.0	40.4
9801	20.7	20.7	20.7	21.2	0.0	14.6	5.0	40.3
9811	20.7	20.7	20.7	21.2	0.0	14.2	5.0	40.3
9820	20.7	20.7	20.7	21.2	0.0	14.2	5.0	40.3
9831	20.7	20.7	20.7	21.2	0.0	11.7	5.0	40.3
9841	20.7	20.7	20.7	21.3	0.0	12.3	5.0	40.3
9850	20.7	20.7	20.7	21.3	0.0	11.6	5.0	40.3
9861	20.7	20.7	20.7	21.3	0.0	11.3	5.0	40.3
9871	20.7	20.7	20.7	21.3	0.0	10.7	5.0	40.3
9880	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
9891	20.7	20.7	20.7	21.2	0.0	9.5	5.0	40.4
9901	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
9911	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
9921	20.7	20.7	20.7	21.3	0.0	8.9	5.0	40.3
9930	20.7	20.7	20.7	21.2	0.0	8.6	5.0	40.3
9941	20.7	20.7	20.7	21.3	0.0	8.5	5.0	40.3
9951	20.7	20.7	20.7	21.2	0.0	8.2	5.0	40.3
9960	20.7	20.7	20.7	21.2	0.0	10.3	5.0	40.3
9971	20.7	20.7	20.7	21.2	0.0	11.6	5.0	40.5
9981	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
9990	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
10001	20.7	20.7	20.7	21.2	0.0	9.7	5.0	40.3

10011	20.7	20.7	20.7	21.2	0.0	9.9	5.0	40.3
10020	20.7	20.7	20.7	21.2	0.0	9.8	5.0	40.3
10031	20.7	20.7	20.7	21.2	0.0	9.6	5.0	40.3
10041	20.7	20.7	20.7	21.2	0.0	9.0	5.0	40.3
10050	20.7	20.7	20.7	21.2	0.0	9.8	5.0	40.3
10061	20.7	20.7	20.7	21.2	0.0	11.5	5.0	40.3
10071	20.7	20.7	20.7	21.2	0.0	12.1	5.0	40.3
10080	20.7	20.7	20.7	21.3	0.0	11.7	5.0	40.5
10091	20.7	20.7	20.7	21.3	0.0	11.4	5.0	40.3
10101	20.7	20.7	20.7	21.2	0.0	10.9	5.0	40.3
10110	20.7	20.7	20.7	21.3	0.0	10.6	5.0	40.3
10121	20.7	20.7	20.7	21.2	0.0	9.9	5.0	40.3
10131	20.7	20.7	20.7	21.2	0.0	11.0	5.0	40.3
10140	20.7	20.7	20.7	21.2	0.0	8.8	5.0	40.3
10151	20.7	20.7	20.7	21.2	0.0	10.2	5.0	40.3
10161	20.7	20.7	20.7	21.2	0.0	10.1	5.0	40.3
10170	20.7	20.7	20.7	21.3	0.0	10.0	5.0	40.3
10181	20.7	20.7	20.7	21.2	0.0	10.3	5.0	40.3
10191	20.7	20.7	20.7	21.2	0.0	7.9	5.0	40.3
10200	20.7	20.7	20.7	21.2	0.0	9.1	5.0	40.3
10211	20.7	20.7	20.7	21.3	0.0	8.7	5.0	40.3
10221	20.7	20.7	20.7	21.2	0.0	7.9	5.0	40.3
10230	20.7	20.7	20.7	21.3	0.0	7.2	5.0	40.3
10241	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
10251	20.7	20.7	20.7	21.2	0.0	9.0	5.0	40.3
10260	20.7	20.7	20.7	21.3	0.0	10.4	5.0	40.2
10271	20.7	20.7	20.7	21.3	0.0	10.4	5.0	40.3
10281	20.7	20.6	20.7	21.2	0.0	9.8	5.0	40.3
10290	20.7	20.7	20.7	21.2	0.0	11.8	5.0	40.3
10301	20.7	20.7	20.7	21.2	0.0	11.7	5.0	40.3
10311	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.3
10320	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.3
10330	20.7	20.7	20.7	21.3	0.0	9.1	5.0	40.3
10341	20.7	20.7	20.7	21.3	0.0	8.9	5.0	40.3
10350	20.7	20.7	20.7	21.3	0.0	8.4	5.0	40.3
10360	20.7	20.7	20.7	21.2	0.0	8.9	5.0	40.3
10371	20.7	20.7	20.7	21.2	0.0	10.3	5.0	40.3
10380	20.7	20.7	20.7	21.2	0.0	11.0	5.0	40.2
10391	20.7	20.7	20.7	21.2	0.0	11.7	5.0	40.2
10401	20.7	20.7	20.7	21.3	0.0	10.8	5.0	40.3
10410	20.7	20.7	20.7	21.2	0.0	9.6	5.0	40.4
10421	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.3
10431	20.7	20.7	20.7	21.2	0.0	9.5	5.0	40.3
10441	20.7	20.7	20.7	21.3	0.0	9.3	5.0	40.3
10450	20.7	20.7	20.7	21.3	0.0	10.3	5.0	40.3
10461	20.7	20.7	20.7	21.2	0.0	13.0	5.0	40.3

10471	20.7	20.7	20.7	21.3	0.0	11.6	5.0	40.3
10480	20.7	20.7	20.7	21.2	0.0	11.0	5.0	40.3
10491	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
10501	20.7	20.7	20.7	21.2	0.0	11.0	5.0	40.3
10510	20.7	20.7	20.7	21.2	0.0	11.1	5.0	40.3
10521	20.7	20.7	20.7	21.3	0.0	11.0	5.0	40.3
10531	20.7	20.7	20.7	21.2	0.0	11.6	5.0	40.3
10540	20.7	20.7	20.7	21.2	0.0	9.5	5.0	40.3
10551	20.7	20.7	20.7	21.3	0.0	11.4	5.0	40.3
10561	20.7	20.7	20.7	21.3	0.0	7.9	5.0	40.4
10570	20.7	20.7	20.7	21.2	0.0	10.5	5.0	40.3
10581	20.7	20.7	20.7	21.3	0.0	11.7	5.0	40.3
10591	20.7	20.7	20.7	21.3	0.0	11.5	5.0	40.3
10600	20.7	20.7	20.7	21.3	0.0	10.4	5.0	40.3
10611	20.7	20.7	20.7	21.2	0.0	8.8	5.0	40.3
10621	20.7	20.7	20.7	21.2	0.0	10.5	5.0	40.3
10630	20.7	20.7	20.7	21.3	0.0	10.3	5.0	40.2
10641	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
10651	20.7	20.6	20.7	21.2	0.0	10.4	5.0	40.3
10660	20.7	20.7	20.7	21.2	0.0	10.7	3.1	40.3
10671	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
10681	20.7	20.7	20.7	21.2	0.0	10.4	5.0	40.4
10690	20.7	20.7	20.7	21.2	0.0	9.6	5.0	40.2
10700	20.7	20.7	20.7	21.2	0.0	8.5	5.0	40.5
10711	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
10720	20.7	20.7	20.7	21.3	0.0	9.1	5.0	40.3
10730	20.7	20.7	20.7	21.2	0.0	10.0	5.0	40.3
10741	20.7	20.7	20.7	21.2	0.0	10.7	5.0	40.3
10751	20.7	20.7	20.7	21.2	0.0	11.8	5.0	40.3
10760	20.7	20.7	20.7	21.3	0.0	10.4	5.0	40.3
10771	20.7	20.7	20.7	21.2	0.0	12.4	5.0	40.3
10781	20.7	20.7	20.7	21.3	0.0	10.0	3.6	40.3
10790	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
10801	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
10811	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.2
10820	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
10830	20.7	20.7	20.7	21.3	0.0	8.8	5.0	40.3
10841	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
10851	20.7	20.7	20.7	21.2	0.0	9.2	5.0	40.3
10860	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
10871	20.7	20.7	20.7	21.2	0.0	10.5	5.0	40.3
10881	20.7	20.7	20.7	21.2	0.0	11.2	5.0	40.3
10890	20.7	20.7	20.7	21.3	0.0	12.0	5.0	40.3
10901	20.7	20.7	20.7	21.2	0.0	11.3	5.0	40.3
10911	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.4
10920	20.7	20.7	20.7	21.2	0.0	10.0	5.0	40.3

10931	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.2
10941	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.4
10950	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
10961	20.7	20.7	20.7	21.2	0.0	8.7	5.0	40.3
10971	20.7	20.7	20.7	21.2	0.0	8.5	0.1	40.3
10980	20.7	20.6	20.7	21.2	-0.1	6.4	5.0	40.3
10991	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.3
11001	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
11010	20.7	20.7	20.7	21.3	0.0	9.5	5.0	40.3
11021	20.7	20.7	20.7	21.2	0.0	9.9	5.0	40.2
11031	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
11040	20.7	20.7	20.7	21.2	0.0	10.3	5.0	40.3
11051	20.7	20.7	20.7	21.2	0.0	10.5	5.0	40.3
11061	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.2
11070	20.7	20.7	20.7	21.2	0.0	10.8	5.0	40.3
11081	20.7	20.7	20.7	21.3	0.0	11.1	5.0	40.3
11091	20.7	20.7	20.7	21.3	0.0	11.1	5.0	40.3
11101	20.7	20.7	20.7	21.3	0.0	10.3	5.0	40.3
11110	20.7	20.7	20.7	21.3	0.0	9.9	5.0	40.3
11120	20.7	20.7	20.7	21.2	0.0	9.0	4.9	40.3
11131	20.7	20.7	20.7	21.2	0.0	8.7	5.0	40.3
11141	20.7	20.7	20.7	21.3	0.0	8.7	5.0	40.3
11151	20.7	20.7	20.7	21.2	0.0	10.8	5.0	40.3
11160	20.7	20.7	20.7	21.3	0.0	10.7	5.0	40.3
11171	20.7	20.7	20.7	21.3	0.0	11.0	5.0	40.3
11181	20.7	20.7	20.7	21.3	0.0	10.3	5.0	40.3
11190	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.4
11201	20.7	20.7	20.7	21.2	0.0	9.3	5.0	40.3
11211	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.3
11220	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.2
11231	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.3
11241	20.7	20.7	20.7	21.2	0.0	9.7	5.0	40.3
11250	20.7	20.7	20.7	21.3	0.0	9.7	5.0	40.3
11261	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.3
11271	20.7	20.7	20.7	21.3	0.0	9.3	0.0	40.3
11280	20.7	20.7	20.7	21.2	0.0	8.4	5.0	40.3
11290	20.7	20.7	20.7	21.3	0.0	8.0	4.7	40.3
11301	20.7	20.7	20.7	21.2	0.0	8.5	5.0	40.3
11310	20.7	20.7	20.7	21.2	0.0	8.9	5.0	40.3
11320	20.7	20.6	20.7	21.3	0.0	8.7	5.0	40.3
11331	20.7	20.7	20.7	21.3	0.0	9.8	5.0	40.3
11340	20.7	20.7	20.7	21.3	0.0	9.4	5.0	40.2
11350	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.2
11361	20.7	20.7	20.7	21.2	0.0	10.9	5.0	40.3
11370	20.7	20.7	20.7	21.2	0.0	11.5	5.0	40.3
11380	20.7	20.7	20.7	21.3	0.0	11.7	5.0	40.3

11391	20.7	20.7	20.7	21.3	0.0	11.3	5.0	40.4
11401	20.7	20.7	20.7	21.3	0.0	9.2	5.0	40.3
11410	20.7	20.7	20.7	21.3	0.0	10.2	5.0	40.3
11421	20.7	20.7	20.7	21.3	0.0	10.1	5.0	40.3
11431	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.2
11440	20.7	20.7	20.7	21.2	0.0	9.7	5.0	40.3
11451	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.3
11461	20.7	20.7	20.7	21.3	0.0	10.5	5.0	40.3
11470	20.7	20.7	20.7	21.3	0.0	9.6	5.0	40.3
11481	20.7	20.7	20.7	21.3	0.0	8.9	5.0	40.3
11491	20.7	20.7	20.7	21.3	0.0	8.4	5.0	40.3
11500	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.3
11511	20.7	20.7	20.7	21.2	0.0	11.0	5.0	40.2
11521	20.7	20.7	20.7	21.3	0.0	12.2	5.0	40.2
11530	20.7	20.7	20.7	21.2	0.0	10.5	5.0	40.3
11541	20.7	20.7	20.7	21.3	0.0	10.8	5.0	40.2
11551	20.7	20.7	20.7	21.3	0.0	10.0	5.0	40.3
11560	20.7	20.7	20.7	21.2	0.0	9.4	5.0	40.2

2nd Dynamic extraction ends at 11560s

11571	20.7	20.7	20.7	21.3	0.0	-0.7	1.7	40.3
11581	20.7	20.7	20.7	21.3	0.0	-0.2	0.8	40.4
11590	20.7	20.7	20.7	21.3	0.0	-0.1	0.1	40.3
11601	20.7	20.7	20.7	21.3	0.0	-0.1	0.4	40.3
11611	20.7	20.7	20.7	21.3	1.7	5.0	1.8	40.3
11620	20.7	20.7	20.7	21.3	0.4	4.4	1.6	40.3

Starts bypassing SC CO_2 through the lines downstream of the vessel

11631	20.7	20.5	20.7	21.3	0.0	14.0	0.0	40.2
11641	20.7	20.7	20.7	21[illegible]	0.0	19.4	0.1	40.2
11650	20.7	20.7	20.7	21.3	0.0	18.7	0.1	40.2
11661	20.7	20.7	20.7	21.3	0.0	23.6	0.1	40.1
11671	20.7	20.7	20.7	21.3	0.0	21.3	0.0	40.2
11680	20.7	20.7	20.7	21.3	0.0	23.2	0.0	40.2
11691	20.7	20.7	20.7	21.3	0.0	20.3	0.0	40.1
11701	20.7	20.7	20.7	21.3	0.0	31.5	0.0	40.1
11710	20.7	20.7	20.7	21.3	0.0	25.0	0.0	40.1
11721	20.7	20.7	20.7	21.3	0.0	24.0	0.0	40.1
11731	20.7	20.7	20.7	21.3	0.0	13.9	0.0	40.1
11740	20.7	20.7	20.7	21.3	0.0	14.6	0.0	40.0
11751	20.7	20.7	20.7	21.2	0.0	14.0	0.0	40.0
11761	20.7	20.7	20.7	21.2	0.0	12.4	0.0	40.0
11770	20.7	20.7	20.7	21.2	0.0	12.1	0.0	40.0
11781	20.7	20.7	20.7	21.2	0.0	11.6	0.0	40.0

End of bypass flow at 11781s, end of double cycle extraction, data acquisition still running

11791	20.7	20.7	20.7	21.2	0.0	-0.8	0.0	40.1
11800	20.7	20.7	20.7	21.2	0.0	-0.2	0.0	40.0
11811	20.7	20.7	20.7	21.3	0.0	-0.2	0.0	40.1
11821	20.7	20.7	20.7	21.2	0.0	-0.1	0.0	40.1
11830	20.7	20.7	20.7	21.2	0.0	0.0	0.0	40.1
11841	20.7	20.8	20.7	21.2	0.0	0.0	0.0	40.0
11851	20.7	20.8	20.7	21.2	0.0	0.0	0.0	40.0
11860	20.7	20.8	20.7	21.2	0.0	0.0	0.0	40.0
11871	20.7	20.8	20.7	21.2	0.0	0.0	0.0	40.0
11881	20.7	20.9	20.7	10.2	0.0	0.0	0.0	36.7
11890	20.7	20.9	20.7	8.2	0.0	0.0	0.0	30.5
11901	20.7	20.9	20.7	7.9	0.0	0.0	0.0	30.1
11911	20.7	20.9	20.7	8.0	0.0	0.0	0.0	30.9
11921	20.7	20.9	20.7	7.8	0.0	0.0	0.0	30.5
11930	20.7	20.9	20.7	7.6	0.0	0.0	0.0	29.7
11941	20.7	20.9	20.7	7.3	0.0	0.0	0.0	27.8
11951	20.7	20.9	20.7	7.0	0.0	0.0	0.0	26.1
11960	20.7	20.9	20.7	6.6	0.0	0.0	0.0	24.7
11971	20.7	20.9	20.7	5.9	0.0	0.0	0.0	22.8
11981	20.7	20.9	20.7	5.6	0.0	0.0	0.0	21.8
11990	20.7	20.9	20.7	5.3	0.0	0.0	0.0	22.0
12001	20.7	20.9	20.7	4.8	0.0	0.0	0.0	22.7
12011	20.7	21.0	20.7	4.1	0.0	0.0	0.0	22.4
12020	20.7	21.0	20.7	2.9	0.0	0.0	0.0	21.0
12031	20.7	21.0	20.7	2.0	0.0	0.0	0.0	19.7
12041	20.7	21.0	20.7	1.4	0.0	0.0	0.0	19.6
12050	20.7	21.0	20.7	1.2	-0.1	0.0	0.0	20.2
12061	20.7	20.9	20.7	0.8	0.0	0.0	0.0	21.4
12071	20.7	20.9	20.7	0.8	0.0	0.0	0.0	22.5
12080	20.7	20.9	20.7	0.7	-0.1	0.0	0.0	23.9
12091	20.7	20.9	20.7	0.7	0.0	0.0	0.0	25.2
12101	20.7	20.9	20.7	0.7	0.0	0.0	0.0	26.4
12110	20.7	20.9	20.7	0.8	0.0	0.0	0.0	27.2
12121	20.7	20.9	20.7	0.7	0.0	0.0	0.0	28.1
12131	20.7	20.9	20.7	0.7	0.0	0.0	0.0	28.7
12140	20.7	20.9	20.7	0.8	0.0	0.0	0.0	29.2
12151	20.7	20.9	20.7	0.8	0.0	0.0	0.0	29.6
12161	20.7	20.9	20.7	0.7	0.0	0.0	0.0	30.0
12170	20.7	20.9	20.7	0.7	0.0	0.0	0.0	30.4
12180	20.7	20.9	20.7	0.7	0.0	0.0	0.0	30.6
12191	20.7	20.9	20.7	0.7	0.0	0.0	0.0	30.9
12200	20.7	20.9	20.7	0.6	0.0	0.0	0.0	31.0
12210	20.7	20.9	20.7	0.7	0.0	0.0	0.0	31.1

12221	20.7	20.9	20.7	0.9	0.0	0.0	0.0	31.3
12231	20.7	20.9	20.7	0.6	0.0	0.0	0.0	31.4
12240	20.7	20.8	20.7	0.9	0.0	0.0	0.0	31.5
12251	20.7	20.8	20.7	0.7	0.0	0.0	0.0	31.5
12261	20.7	20.8	20.7	0.6	0.0	0.0	0.0	31.6
12270	20.7	20.8	20.7	0.8	0.0	0.0	0.0	31.6
12281	20.7	20.8	20.7	0.7	0.0	0.0	0.0	31.7
12291	20.7	20.8	20.7	0.7	0.0	0.0	0.0	31.7
12300	20.7	20.8	20.7	0.5	0.1	0.0	0.0	31.8
12311	20.7	20.8	20.7	0.7	0.1	0.0	0.0	31.9
12321	20.7	20.8	20.7	0.7	0.1	0.0	0.0	31.9
12330	20.7	20.8	20.7	0.5	0.0	0.0	0.0	32.0
12340	20.7	20.8	20.7	0.8	0.0	0.0	0.0	32.0
12351	20.7	20.8	20.7	0.7	0.0	0.0	0.0	32.1
12360	20.7	20.8	20.7	0.7	0.0	0.0	0.0	32.2
12371	20.7	20.7	20.7	0.7	0.0	0.0	0.0	32.2
12381	20.7	20.7	20.7	0.9	0.0	0.0	0.0	32.3
12390	20.7	20.7	20.7	0.9	0.0	0.0	0.0	32.3
12401	20.7	20.7	20.7	0.8	0.0	0.0	0.0	32.3
12411	20.7	20.7	20.7	0.7	0.0	0.0	0.0	32.3
12420	20.7	20.7	20.7	0.8	0.0	0.0	0.0	32.4
12431	20.7	20.7	20.7	0.7	0.0	0.0	0.0	32.4
12441	20.7	20.7	20.7	0.6	0.0	0.0	0.0	32.5
12450	20.7	20.7	20.7	0.7	0.0	0.0	0.0	32.5
12460	20.7	20.7	20.7	0.7	0.0	0.0	0.0	32.5
12471	20.7	20.7	20.7	0.8	0.0	0.0	0.0	32.6
12480	20.7	20.7	20.7	0.6	0.0	0.0	0.0	32.6
12490	20.7	20.7	20.7	0.8	0.0	0.0	0.0	32.6
12501	20.7	20.6	20.7	0.7	0.0	0.0	0.0	32.6
12510	20.7	20.6	20.7	0.7	0.0	0.0	0.0	32.6
12520	20.7	20.6	20.7	0.8	0.0	0.0	0.0	30.9
12531	20.7	20.6	20.7	0.7	0.0	0.0	0.0	29.4
12540	20.7	20.6	20.7	0.7	0.0	0.0	0.0	28.3
12550	20.7	20.6	20.7	0.8	0.0	0.0	0.0	27.6
12561	20.7	20.6	20.7	0.6	0.0	0.0	0.0	27.1
12571	20.7	20.6	20.7	0.7	0.0	0.0	0.0	26.7
12580	20.7	20.6	20.7	0.8	0.0	0.0	0.0	26.6
12591	20.7	20.6	20.7	0.7	0.0	0.0	0.0	26.6
12601	20.7	20.6	20.7	0.7	0.0	0.0	0.0	26.7
12610	20.7	20.5	20.7	0.6	0.0	0.0	0.0	26.6
12621	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.8
12631	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12640	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12651	20.7	20.5	20.7	0.7	0.0	0.0	0.0	27.0
12661	20.7	20.5	20.7	0.7	0.0	0.0	0.0	27.0
12670	20.7	20.5	20.7	0.7	0.0	0.0	0.0	27.0

12681	20.7	20.5	20.7	0.9	0.0	0.0	0.0	27.1
12691	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12700	20.7	20.5	20.7	0.8	0.0	0.0	0.0	26.8
12711	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12721	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12730	20.7	20.5	20.7	0.7	0.0	0.0	0.0	26.9
12740	20.7	20.4	20.7	0.7	0.0	0.0	0.0	26.9
12751	20.7	20.4	20.7	0.8	0.0	0.0	0.0	26.9
12761	20.7	20.4	20.7	0.7	0.0	0.0	0.0	26.9
12770	20.7	20.4	20.7	0.7	0.0	0.0	0.0	26.9
12781	20.7	20.4	20.7	0.7	0.0	0.0	0.0	26.9
12791	20.7	20.4	20.7	0.7	0.0	0.0	0.0	27.0
12800	20.7	20.4	20.7	0.7	0.0	0.0	0.0	26.9

LabView data acquisition stopped

APPENDIX C

Appendix C: Areas obtained for Calibration verification standards (1000, 5000 ppm)

Calibration verification standard (1000 ppm)

Sample batch run #	**AREA**				**Drift**	
	1st injection	2nd injection	3rd injection	Average	%	Average
1	3115700	2846711	3042213	3001541	17..9	**2.4**
2	3471063	3996018	3476557	3647879	0.3	
3	2982712	3428240	3084218	3165057	13.4	
4	4430956	3088856	3331467	3617093	1.1	
5	3989307	3860109	3913062	3920826	-7.2	
6	3647879	3589662	4002051	3746531	-2.4	
7	3849830	3658972	3999564	3836122	-4.9	
8	3378943	2856310	3056981	3097411	15.3	
9	3622458	3520001	3984233	3708897	-1.4	
10	3994258	3200012	3564002	3586091	1.9	
11	3955262	-	-	3955262	-8.1	
Calibration verification standard (5000 ppm)						
12	10807138	11535730	11403650	11254437	5.2	**-3.4**
13	12786423	13358002	15682281	13942235	-17.5	
14	10023560	11135802	12118980	11092781	6.5	
15	13897012	12998654	12879432	13258366	-11.7	
16	10889423	11876541	12579432	11781799	0.7	

The above table shows the raw data (in terms of area) obtained for each of the calibration verification standards (1000 ppm, 5000 ppm) while running batches of sample analyses. The areas shown in the table are compared to the actual areas obtained during the GC calibration for 1000 ppm (= 3657697 area counts) calibration verification standard and 5000 ppm (= 11868109 area counts) calibration standard. If the % drift is >20%, the GC is recalibrated.

APPENDIX D

Appendix D: Calculation for expected amount of water based on solubility of water

Table D1-1: **Calculation of expected amount of moisture content extracted at each extraction condition based on the solubility of water at those extraction conditions**

MPa	Temp. (^oC)	Density of CO_2 (g/mL)	GSL Solubility of water (mole/mole)	g of CO_2	Moles of CO_2	Moles of water	g of water extracted in double cycle	g of HCs+water extracted	% Recovery	Expected % extraction based on HCs mass collected
11.0	40	0.69	3.49E-06	677.84	15.41	5.38E-05	9.68E-04	1.50	102	104
11.0	40	0.69	3.49E-06	644.09	14.64	5.11E-05	9.20E-04	1.30	88	90
12.4	40	0.73	6.53E-06	517.85	11.77	7.69E-05	1.38E-03	1.32	89	91
12.4	40	0.73	6.53E-06	607.97	13.82	9.02E-05	1.62E-03	1.62	110	112
13.8	40	0.76	9.94E-06	527.97	12.00	1.19E-04	2.15E-03	1.42	96	98
13.8	40	0.76	9.94E-06	601.07	13.66	1.36E-04	2.44E-03	1.12	76	78
13.8	40	0.76	9.94E-06	692.18	15.73	1.56E-04	2.81E-03	1.04	70	72
15.2	40	0.78	1.37E-06	663.85	15.09	2.06E-05	3.71E-04	1.87	127	130
15.2	40	0.78	1.37E-06	653.82	14.86	2.03E-05	3.65E-04	1.62	110	112
15.2	40	0.78	1.37E-06	785.09	17.84	2.44E-05	4.39E-04	1.29	88	89
20.7	40	0.85	3.16E-05	660.17	15.00	4.74E-04	8.54E-03	1.80	121	124
20.7	40	0.85	3.16E-05	615.02	13.98	4.42E-04	7.95E-03	1.54	104	107
24.1	**40**	**0.87**	**4.51E-05**	**653.09**	**14.84**	**6.69E-04**	**1.20E-02**	**1.58**	**106**	**109**
24.1	40	0.87	4.51E-05	664.81	15.11	6.81E-04	1.23E-02	1.62	109	112
15.2	40	0.78	1.37E-06	1387.71	31.54	4.31E-05	7.75E-04	3.02	206	209
15.2	40	0.78	1.37E-06	1971.26	44.80	6.12E-05	1.10E-03	2.74	186	120
15.2	40	0.78	1.37E-06	817.67	18.58	2.54E-05	4.57E-04	1.43	97	98
15.2	40	0.78	1.37E-06	864.57	19.65	2.68E-05	4.83E-04	0.83	57	58
15.2	40	0.78	1.37E-06	384.44	8.74	1.19E-05	2.15E-04	0.60	41	42
15.2	40	0.78	1.37E-06	493.51	11.22	1.53E-05	2.76E-04	0.76	52	53

g of SC CO_2 shown in Table F2-1 were obtained by summing up the amount of SC CO_2 passing through the vessel during every 5 minutes of each of the two-30 minutes dynamic extractions.

Moles of CO_2 = g CO_2/44
Where, 44 is the molecular weight of CO_2

Moles of water = solubility of water (moles water/mole CO_2)*moles CO_2

Thus, g of water extracted = moles of water*18
Where, 18 is the molecular weight of water

SAMPLE CALCULATION (at 24.1MPa, 40°C –run1)

Solubility of water at 24.1MPa and 40°C = 4.51E-05 moles water/moles CO_2

g of SC CO_2 as obtained from cumulating mass of SC CO_2 passed during total dynamic extraction (see Table C6-3) = 653.09 g

Moles of CO_2 = 653.09/44 = 14.84 moles CO_2

Moles of water = (4.51E-05 moles water/moles CO_2)/ 14.84 moles CO_2

= 6.69E-04 moles water

⇒ g of water extracted = 6.69E-04 moles water* 18 g water/mole water

= 1.2E-02 g water extracted

APPENDIX E

Appendix E: Sample calculation for expected % extraction
(at 24.1MPa, 40°C – run1)

SAMPLE CALCULATION

Since, g of SC CO_2 at 24.1 MPa in pumps (at 7.5°C) = g of SC CO_2 at 24.1 MPa in the vessel (at 40°C)

SC CO_2 density at 24.1 MPa and 7.5°C = 1.0077g

Amount of PHCs present in contaminated flare pit soil 1 = 31774 mg/Kg (or 3.1774 g in 1000 g)

Amount of flare pit soil 1 in the vessel = 50.0282 g

Dry weight of soil in the vessel (based on 9.05% moisture content) = 45.52566 g

⇒ Amount of HCs expected to be present in the 45.53 g of soil that could be extracted $= \frac{31.774 \text{ g HCs} * 45.52566\text{g soil}}{1000 \text{ g soil}} = \mathbf{1.4465g}$

Amount of HCs+water extracted during this extraction = 1.58 g (see Table F-2)

% Expected extraction based on mass of HCs collected = 1.58 g /1.4465 g

= **109.2 %**

APPENDIX F

APPENDIX F1

Appendix F1: ANOVA for Double Cycle extraction runs at 40°C (with efficiencies from 81 to 89%)

To test if there is a difference between the obtained PHC means and therefore, the extraction efficiency for the SC CO_2 extractions at 40°C with pressures ranging from 13.8MPa to 24.1MPa, an analysis of variance (ANOVA) of the extraction runs within this range was done. Each group in Table F1-1 represents an extraction condition investigated (with extraction efficiency determined as between 81 and 90%), while the "count" is the number of mean PHC content obtained for each run.

Table F1-1: ANOVA for Double Cycle runs at 40°C from 13.8MPa to 24.1MPa (with efficiencies from 81 to 90%)

Groups	Count	Sum	Average	Variance		
13.8MPa, 40°C	3	19209	6403	4200241		
15.2MPa, 40°C	3	16466	5489	3670540		
20.7MPa, 40°C	2	7488	3744	250625		
24.1MPa, 40°C	2	6333	3167	24024		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	16472367	3	5490789	**2.057**	0.207	**4.757**
Within Groups	16016212	6	2669369			
Total	32488579	9				

At $\alpha=0.05$ (i.e. at 95% confidence level)

Since the Fcritical>Fcalculated (i.e. 4.757 > 2.057), there is no difference between the means of the PHC content from one SC CO_2 extraction condition to another (for extractions done from 13.8MPa to 24.1 MPa).

Appendix F2

Appendix F2: ANOVA for Double Cycle extraction runs at 60°C for flare pit soil 1 and at 40°C for flare pit soil 2

To test if there is a difference between the obtained PHC means and therefore, the extraction efficiency for the SC CO_2 extractions at 60°C with pressures ranging from 12.4MPa to 15.2MPa, an analysis of variance (ANOVA) of the extraction runs within this range was done. Each group in Table F2-1 is represent an extraction condition investigated, while the "count" is the number of mean PHC content obtained for each run.

Table F2-1: ANOVA for Double Cycle extractions at 60°C with pressures ranging from 12.4MPa to 15.2MPa (flare pit soil 1)

Groups	Count	Sum	Average	Variance		
12.4MPa, 60oC	2	31605	15802	526948		
13.1MPa, 60oC	2	31374	15687	4218018		
15.2MPa, 60oC	2	13941	6970	3701761		
ANOVA						
Source of Variatiom	SS	df	MS	F	P-value	**F crit**
Between Groups	1.03E+08	2	51331377	**18.231**	0.021	**9.552**
Within Groups	8446726	3	2815575			
Total	1.11E+08	5				

At $\alpha=0.05$ (i.e. at 95% confidence level)

Since the Fcalculated >Fcritical (i.e. 18.231 > 9.552), there is a significant difference between the means of the PHC content from one SC CO_2 extraction condition to another (for extractions done from 12.4MPa to 15.2 MPa).

To test if there is a difference between the obtained PHC means and therefore, the extraction efficiency for the SC CO_2 extractions at 40°C for FP 2 with pressures ranging from 13.8MPa to 24.1MPa, an analysis of variance (ANOVA) of the extraction runs within this range was done. Each group in Table F2-2 is represent an extraction condition investigated, while the "count" is the number of mean PHC content obtained for each run.

Table F2-2: ANOVA for Double Cycle extractions at 40°C with pressures ranging from 13.8MPa to 24.1MPa (FP 2)

Groups	Count	Sum	Average	Variance		
13.8MPa, 40oC	2	92745	46372	3308211		
14.8MPa, 40oC	2	77174	38587	5935594		
24.1MPa, 40oC	2	46917	23459	1505266		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	**F crit**
Between Groups	5.43E+08	2	2.72E+08	**75.777**	0.003	**9.552**
Within Groups	10749071	3	3583024			
Total	5.54E+08	5				

At $\alpha=0.05$ (i.e. at 95% confidence level)

Since the Fcalculated >>Fcritical (i.e. 75.777 >> 9.552), there is a significant difference between the means of the PHC content from one SC CO_2 extraction condition to another (for extractions done from 13.8MPa to 24.1 MPa).

APPENDIX F3

Appendix F3: ANOVA for Double Cycle Extractions with different SC CO_2 densities (0.43 to 0.87 g/mL) at 40°C and at flowrates of 1mL/min, 5mL/min and 20mL/min (at 15.2MPa, 40°C)

To test if there is a difference between the mean PHC hydrocarbon content (and subsequently the extraction efficiencies) obtained for the double cycle extractions at different SC CO_2 densities ranging from 0.43 g/mL (at 15.2 MPa and 80°C) to 0.87 g/mL (at 24.1 MPa and 40°C), an ANOVA test was carried out as shown below. Each group represents the SC CO_2 extraction densities at which the experiment was run, while "count" is the number of mean PHC contents obtained for each of the 6 sub-samples (3 sub-samples per batch of extraction run, 6 sub-samples for 2 runs at the same conditions).

Table F3-1: ANOVA for extractions at different flowrates (at 15.2MPa, 40°C)

Groups	Count	Sum	Average	Variance		
0.43 g/mL	2	90	45	36		
0.47 g/mL	2	92	46	6		
0.51 g/mL	2	93	47	49		
0.61 g/mL	2	153	76	43		
0.68 g/mL	2	140	70	1		
0.73 g/mL	2	144	72	1		
0.76 g/mL	2	152	76	59		
0.78 g/mL	2	157	79	43		
0.85 g/mL	2	174	87	3		
0.87 g/mL	2	178	89	0		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5085.36	9	565.04	**23.55**	0.00	**3.02**
Within Groups	239.90	10	23.99			
Total	5325	19				

At α=0.05 (i.e. at 95% confidence level)

Since the Fcritical << F calculated (i.e. 3.02<< 23.55), there is a significant difference between the means of the PHC content for the double cycle extractions at different SC CO_2 densities showing that the process is solvent density dependent.

To test if there is a difference between the mean PHC hydrocarbon content (and subsequently the extraction efficiencies) obtained for the double cycle extractions at different SC CO_2 flowrates of 1 ml/min, 5 mL/min and 20 mL/min (at 15.2 MPa and 40°C), an ANOVA test was carried out as shown below. Each group represents the SC CO_2 extraction flowrates at which the experiment was run, while "count" is the number of mean PHC contents obtained for each of the 6 sub-samples (3 sub-samples per batch of extraction run, 6 sub-samples for 2 runs at the same conditions).

Table F3-2: ANOVA for extractions at different flowrates (at 15.2MPa, 40°C)

Groups	Count	Sum	Average	Variance
20mL/min	6	44702	7450	14236710
5mL/min	6	48932	8155	12440184
1mL/min	6	40257	6709	1129850

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6272828	2	3136414	**0.338**	0.718	**3.682**
Within Groups	1.39E+08	15	9268915			
Total	1.45E+08	17				

At α=0.05 (i.e. at 95% confidence level)

Since the Fcritical > F calculated (i.e. 3.682 > 0.338), there is no difference between the means of the PHC content for the double cycle extractions at different flowrates provided at least 500g of CO_2 is passed through the vessel at 15.2MPa and 40°C.

APPENDIX F4

Appendix F4: ANOVA for flare pit soil 1' Sub-samples PHC Content

For the data shown in Table 4.13, the analysis of the variance in the results obtained for each FP 1 sub-sample analyzed is presented below. ANOVA analysis was performed to investigate if there is any difference (at 95% confidence level) between the mean of the values from one flare pit soil sub-sample to another obtained in each of the two extraction runs. The "groups" in the table below therefore represents each of the 3 sub-samples obtained from the particular extraction run, while the "count" is the number of GC injections for each sub-sample.

Table F4-1: ANOVA for 04-Jul-03 flare pit soil 1 sub-sample batch 1 (15.2MPa and 40°C)

Groups	*Count*	*Sum*	*Average*	*Variance*
04-Jul-03, sub-sample 1	3	27394	9131	50609879
04-Jul-03, sub-sample 2	3	19709	6570	51282516
04-Jul-03, sub-sample 3	3	17521	5840	8201865

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17923798	2	8961899	**0.244**	0.791	**5.143**
Within Groups	220188520	6	36698087			
Total	238112318	8				

At α=0.05 (i.e. at 95% confidence level)

Since the Fcritical>Fcalculated (i.e. 5.143>0.244), there is no significant difference between the means of the PHC content from one sub-sample batch to another for the 04-Jul-03 run.

Table F4-2: ANOVA for 14-Jul-03 flare pit soil 1 sub-sample batch 2 (15.2MPa and 40°C)

Groups	*Count*	*Sum*	*Average*	*Variance*
14-Jul-03, sub-sample 1	3	17521	5840	8201865
14-Jul-03, sub-sample 2	3	24128	8043	20211270
14-Jul-03, sub-sample 3	3	23187	7729	17976146

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8515480	2	4257740	**0.275**	0.768	**5.143**
Within Groups	92778563	6	15463093			
Total	1.01E+08	8				

At α=0.05 (i.e. at 95% confidence level)

Since the Fcritical>Fcalculated (i.e. 5.143 < 0.275), it can be concluded that there appears to be no significant difference within the means for the three groups from. There is therefore no significant difference between the means of the PHC content from one sub-sample to another for the extraction run on 14-Jul-03.

ANOVA analyses for the sub-sample batches obtained at each extraction run performed on 04-Jul-03 and 14-Jul-03 suggests that there is no a significant difference between the means of the PHC hydrocarbon content from one sub-sample batch to another for FP 1.

APPENDIX F5

Appendix F5: ANOVA for 04-Jul-03 and 14-Jul-03 Extractions (15.2MPa and 40°C)

To investigate if there is any difference (at 95% confidence level) between the mean values of the PHC contents obtained on 04-Jul-03 and 14-Jul-03 SC CO_2 extraction runs (performed at the same extraction conditions), the ANOVA analysis for the variance in the results obtained for each SC CO_2 extraction is presented in Table F5-1. Each group therefore includes all the GC injection results (9 GC injections in total) obtained for each day.

Table F5-1: ANOVA for 04-Jul-03 and 14-Jul-03 Extractions (15.2MPa and 40°C)

Groups	*Count*	*Sum*	*Average*	*Variance*		
04-Jul-03, Run1	9	64624	7180	29764040		
14-Jul-03, Run2	9	64836	7204	12661755		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2480	1	2480	**0.00012**	0.992	**4.494**
Within Groups	339406360	16	21212898			
Total	339408841	17				

At α=0.05 (i.e. at 95% confidence level)

Again, since the Fcritical>F (i.e. 4.494 > 0.00012), there is no difference between the means of the PHC content obtained from two different runs performed on 04-Jul-03 and 14-Jul-03 at same SC CO_2 extraction conditions. Thus it can be concluded that the extraction run 1 results are not different from extraction run 2 results.

APPENDIX G

Appendix G Raw data for cumulative mass of HCs collected during SC CO_2 extraction

Table G-1: Cumulative mass of HCs collected with Cumulative mass of SC CO_2

Run Time (min.)	Total flow (ml/min)	Volume of CO_2 (mL)	Mass of CO_2 (g)	Cumulative mass of CO_2 (g)	Mass of HCs collected (g)	Cumulative mass of HCs collected (g)
0						
60						
65	11.20	56.00	56.43	56.43	0.1427	0.1427
70	8.60	43.02	43.35	99.79	0.2040	0.3467
75	10.09	50.46	50.85	150.64	0.1415	0.4882
80	9.99	49.97	50.36	201.00	0.1067	0.5949
85	10.33	51.64	52.04	253.03	0.1552	0.7501
90	10.40	51.98	52.38	305.41	0.1041	0.8542
BYPASS 1	15.35	33.15	33.40	338.82	0.058	0.9122
150						
155	6.13	30.66	30.90	369.72	0.1041	1.0163
160	8.45	42.27	42.59	412.31	0.1099	1.1262
165	8.53	42.66	42.98	455.30	0.1088	1.2350
170	9.69	48.47	48.85	504.14	0.0758	1.3108
175	9.66	48.32	48.69	552.83	0.0979	1.4087
180	9.81	49.04	49.42	602.25	0.1433	1.5520
BYPASS 2	20.18	50.45	50.84	**653.09**	0.0284	**1.5804**